MECHANISM OF DELAMINATION OF ELECTROSPUN ADHESIVE NANOFIBERS

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MECHANISM OF DELAMINATION OF ELECTROSPUN ADHESIVE NANOFIBERS

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Thesis

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ABSTRACT

The increasing demand for repositionable adhesive materials has developed a big interest among the scientific and industrial community, electrospun nanofibers has been introduced to the adhesion world as a new material that can provide repositionable dry adhesion.

Adhesion tests were carried to the material, and it was found a unique combination in the adhesive properties presenting a shear adhesion of 29.44 N/cm^2 and a peel strength of 0.06 and 0.01 N/cm^2 for 90° and 180° angles respectively.

It was found that the morphology of the electrospun nanofibers and the porosity of the fiber membrane has an important role into the delamination process along with the interaction between the electrospun fibers and the surface morphology of the substrate.

This research work aims to study how this novel adhesive material delaminates and the factors involved in the delamination process.

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I waited patiently for the LORD; and he inclined unto me, and heard me. Psalms 40:1

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CHAPTER I

INTRODUCTION

Since ancient time, mankind has been using different methods and techniques to join materials, in the search to fulfill different necessities. The use of adhesives have been approximately dated back to 200,000 years ago [1-2].

Many centuries after the first registered use of a material as an adhesive, we are still using them as part of our everyday life from the post-it notes to aerospace industry.

The industrial and technological advances of the modern world promote the research, development and understanding of adhesion and new adhesive materials. "Adhesion refers to the state in which two dissimilar bodies are held together by intimate interfacial contact such that mechanical force or work can be transferred across the interface. These interfacial forces may be caused by electrostatic attraction, chemical bonding, capillary forces or van der Waals interactions" [3].

The growing demand in the adhesives industry has led to the development of materials that provide very strong bonds between surfaces. However, in this type of bonding, their adhesion mechanisms are not reversible: once applied, it is not possible to remove it without damaging the surface of the substrate.

The van der Waals interactions between surfaces has been the focus of study to develop a synthetic reusable adhesive; mimicking how animals and insects in nature can adhere to a wide variety of surfaces, an unlimited number of times [4-7].

This research aims to study how the electrospun nanofibers dry adhesive delaminates from a substrate surface.

CHAPTER II

LITERATURE REVIEW

2.1 Adhesives Overview:

A material that is capable to join two similar or dissimilar surfaces and hold it together, resisting separation, can be defined as an adhesive [3].

Adhesives, bond materials creating a whole system that is greater than the sum of its parts. They are small in volume compared to metals, glass, wood or other materials that they join together.

The use of adhesives has given great advantages on many different types of industries. With the use of adhesive materials, lighter and stronger assemblies are obtained than with mechanical fastening. For example airplane wings, and fuselages can be constructed of a composite material with a honeycomb core structure, bonded to thin faces of aluminum or magnesium.

Adhesives as materials can be can classified in many different ways, broadly by their source (natural or synthetic), and more specifically by their chemical composition (thermosetting, thermoplastic, elastomeric, and adhesive alloys); by their function (structural and non-structural); by their physical form (liquid, paste, films, granular) by their activation and curing method (heat activated, light/UV activated, moisture activated,

chemically activated, solvent based systems, water based systems, pressure sensitive and dry adhesives).

All of these adhesives can be categorized into three different categories: adhesives which harden by chemical reaction, adhesives which harden without chemical reaction and adhesives which do not harden.

Table 2.1 Classification of adhesive materials.

Adhesives	Source	Natural	Synthetic
	Chemical composition	Thermosetting Elastomeric	Thermoplastic Adhesive alloys
	Functionality	Structural	Non-structural
	Physical form	Liquid Films	Paste Solid or granular
	Activation and curing method	Heat activated Light/UV activated Moisture activated Chemically activated Solvent-water based systems	Pressure sensitive Dry adhesives

2.1.1 Adhesives Which Harden by Chemical Reaction

Chemically cured adhesives are reactive materials that require chemical reactions to obtain their adhesion strength. Essentially adhesives of this type are based on a series of monomers which react chemically to produce polymeric structures.

These adhesives can be subdivided into two groups: one-component systems (which includes moisture and heat activated cure categories) and two-component systems (which are subdivided into mix-in and no-mix systems) [16].

Table 2.2 One and Two-component Chemically Cured Adhesives Mayor Sub-classes.

System	Mayor sub-classes	Curing
One-component	Anaerobic	Cures under the absence of oxygen
	Cyanoacrylates	Fast curing, limited in temperature and chemical resistance.
	Heat cured	Cold curing: Room temperature. Warm curing: below 100°C. Hot curing: Above 100 °C, below 288 °C [17].
	Moisture cured	Cure on exposure to moisture. The curing reaction takes place from 5 to 40 °C, with a relative humidity of 40 to 70%.
	Radiation cured	Curing reaction process takes place with light waves of a defined wavelength, radiation and controlled exposure time.
	Silicones	Activated by atmospheric moisture. Requires a relative humidity from 5 to 95%, and temperatures from 5 to 40°C. Complete curing depends on the thickness of the adhesive layer.
Two-component	Epoxies	Resin based systems that is cross linked by a curing agent or hardener.
	Methyl methacrylates	Cures by free radicals mechanism. Polymerization occurs at room temperature [18].
	Silicone adhesives	Cures by a catalyst agent or UV light. Have no issue with thickness and curing process can be accelerated by a temperature gradient.
	Urethanes	Cures by polymerization.

2.1.2 Adhesives Which Harden Without Chemical Reaction

Adhesives which harden without chemical reaction are also called physically hardening adhesives, which refers to the curing process not based on chemical reactions.

On application, this adhesives are presented in their final chemical state, polymers that can be liquefied are used for this. The curing process could be by evaporation or vaporization of solvents, by atmospheric factors or by cooling. Particularly thermoplastics that can be melted, soluble thermoplastics and elastomers, or polymer dispersions are used in this category.

Table 2.3 Physically Cured Adhesives Mayor Sub-classes.

System	Mayor sub-classes	
Hot melts	Rods	Thermoplastic polymers extruded as a rod, applied at 175 °C to 220°C
	Granular, powder	Thermoplastic polymers, supplied as pellets or powder.
	Films	Formulated from synthetic polymers, supplied in different thicknesses.
Organic solvent adhesives	Wet bonding	Solvent based adhesive, strength of the bond depends upon the polymer system in formulation and evaporation of the solvent
	Contact adhesives	Solvent and water based dispersion systems. Can be applied by spray, rolling or direct to the surface. Curing process can be accelerated with the use of a drying oven
Plastisols		Polyvinilchloride particles dispersed in plasticizer. The mixture must be heated from 150°C to 180°C in order to convert the two-phase system to a single-phase.
Water-based adhesives	Solutions	Based on natural and synthetic polymers that can be dissolved in water. Curing occurs by evaporation of water or by absorption into the substrate.
	Polymer dispersions / emulsions	Heterogeneous polymer systems comprising a solid polymer phase in an aqueous phase

2.1.3 Adhesives Which Do Not Harden

Adhesives which do not harden or pressure-sensitive adhesives can be defined as: a continuous flexible strip of cloth, paper, metal or plastic coated on one or both sides with a permanently tacky adhesive; which can adhere to a variety of surfaces.

These coatings are viscous polymeric fluids with a glass transition temperature below room temperature [19-20]. As a result, they remain permanently tacky and have the ability to wet surfaces during contact, the flexibility of the backing and application of light pressure contributes to the adherend wetting.

If inadequate pressure is applied or temperature is too low, bonding flaws such as bubbles or detachment can occur, the ones could promote cavitation and failure of the bond [21]. Generally PSAs can be broadly classified by their chemical composition, adhesive system, and by their construction.

Table 2.4 Pressure Sensitive Adhesives Classification by Chemical Composition.

Chemical composition	Rubber based	Based on natural or synthetic rubbers formulated with tackifiers. Provides good to excellent initial tack. Does not provide good resistance to high temperature, chemical agents and ultraviolet rays.
	Acrylics	Formulated from cross-linked acrylic polymers; They exhibit a stronger bond than rubber based formulations. Also provides good resistance to high temperature, oxidation, and chemical agents. Provides a low initial tack and takes a longer time to obtain their maximum adhesion.

	Modified acrylics	Formulated from acrylic polymers but incorporating tackifying resins and additional components found in rubber-based systems. Modified acrylics exhibit high initial tack, good bonding to low-energy surfaces, but low resistant to chemical agents and ultraviolet rays.
	Silicone based	Formulated with silicone polymers. Exhibits good adhesion properties to silicone substrates. Provides higher temperature resistance than rubber and acrylic based adhesives, but presents low initial tack and higher cost.

Table 2.5 Pressure Sensitive Adhesives Classification by Adhesive System and Construction.

Adhesive system	Solvent	Acrylic polymers in solvent based processes. Once diluted, they are applied to a facestock. After coating, the solvent evaporates leaving the adhesive layer.
	Hot melt	Rubber based thermoplastics compounded with tackifying resins. The coating process is performed in temperatures up to 150°C
	Emulsion	Rubber or acrylic based, the adhesives are emulsified in water for coating.
	UV	Light-cured acrylics, non-flammable and solvent free.
Construction	Single coated	The adhesive is coated on one side of the backing or facestock.
	Double coated	The adhesive is coated to both sides of the facestock. The adhesive layer maybe of the same or different type and of variable thickness. Generally includes a release liner.
	Reinforced	Single or double coated adhesives which in addition to the facestock includes a reinforcement layer.
	Unsupported	Unsupported layer of adhesive that is coated on a release line, commonly paper with silicone release agents.
	Self-wound	A carrier which is coated on one side with PSA and on the other with a release coating. There is no release liner with these types of products.

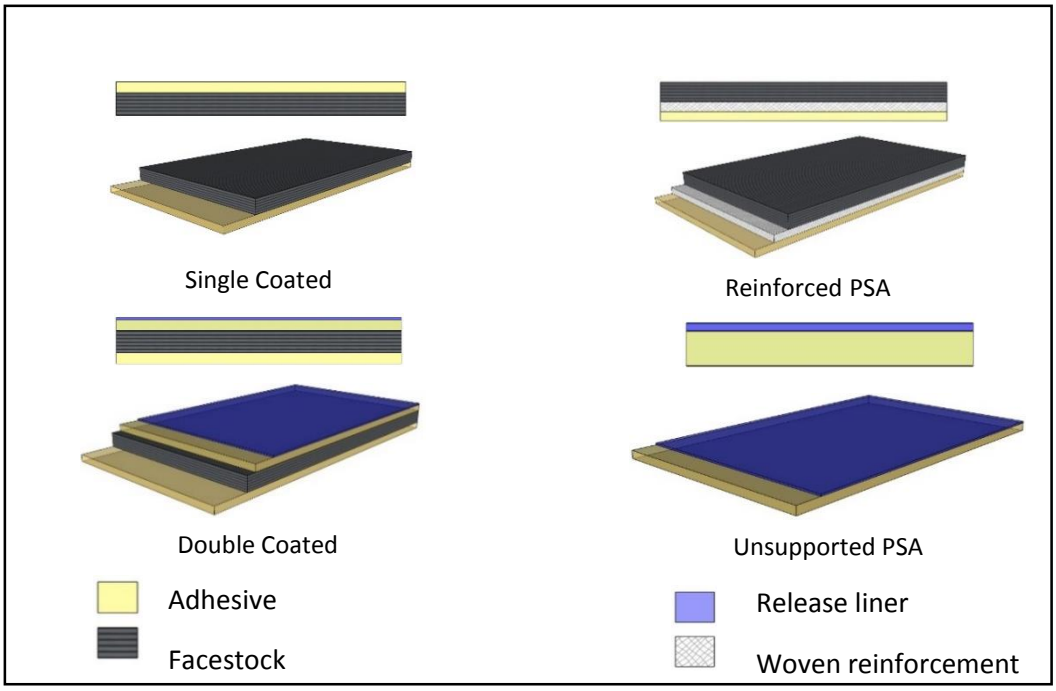


Figure 2.1 Most Common PSAs Construction.

2.2 Nature-Inspired Dry Adhesives

The evolution of biological organisms over millions of years have allowed nature to optimize methods, mechanisms and processes thru experimentation and natural selection in areas such as physics, chemistry, materials science, mechanics among many others.

Biologically adhesives have an impressive performance in their natural context; being capable of accomplishing feats that are unmatched by synthetic adhesives [24, 25]. Adhesion in nature can be categorized broadly into three major categories: dry adhesion, reversible wet adhesion and chemical adhesion [26].

Dry adhesion is a reversible adhesion mechanism that relies mainly on the van der Waals forces and the close interaction between the attaching structure and the substrate without wetting the surface [27].

This mechanism has attracted much attention from the industrial and scientific community, because it provides considerable strong, but reversible attachment to a variety of surface with different roughness, even orientation.

Reversible wet adhesion differs from dry adhesion due to the wetting of the attaching structure to the substrate. The adhesion force is generated essentially by increasing the viscosity and surface tension around the contact area, in essence capillary forces [28].

Chemical adhesion or permanent adhesion which are exhibited on mussels adhering to different surfaces through the secretion of natural adhesive proteins. These proteins cross-link with each other to form a stable, strong bond [29, 30].

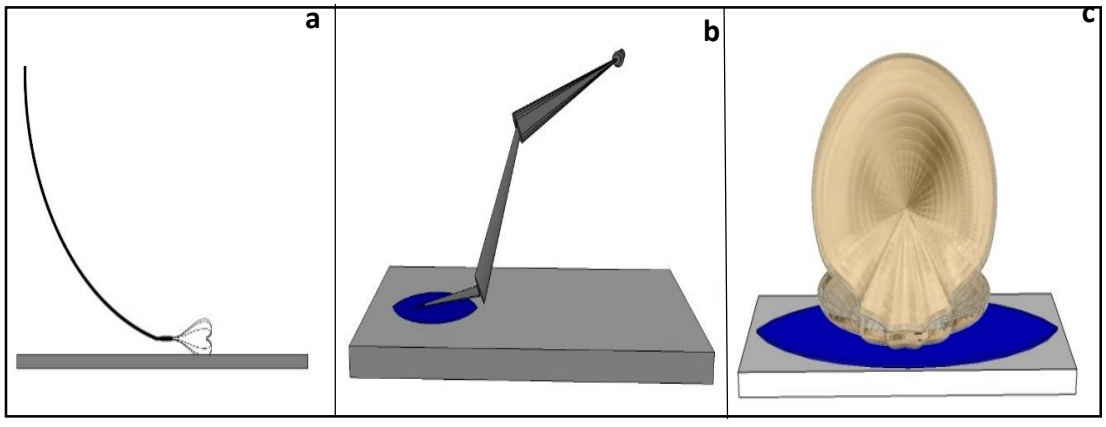


Figure 2.2 Schematic illustration of dry, reversible wet and permanent adhesion mechanisms. **a)** Dry adhesion between a gecko setae and substrate. **b)** Reversible wet

adhesion of a stick insect tarsus and substrate. **c)** permanent wet adhesion of mussel and substrate.

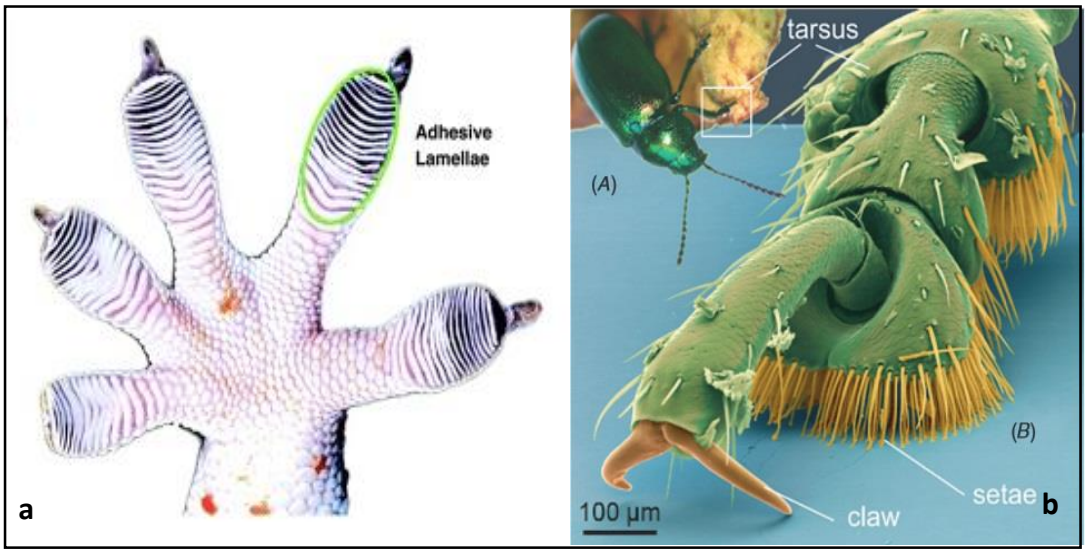


Figure 2.3 Examples of dry and wet reversible adhesion in nature. **a)** Gecko feet (dry) [31]. **b)** Tarsus of the crysomelid beetle (wet) [32].

Within the three major categories of natural adhesives, we can find different subdivisions of adhesion mechanisms. These are not mutually exclusive. In biological systems, more than one mechanism can be present: wet adhesion, hooks, lock, suction cups, dry adhesion, clamps, spacers and friction [33].

The ones that can have the following physical effects involved: electrostatic forces, van der Waals forces, capillary effect, chemical bonding, viscous forces, muscular forces and friction.

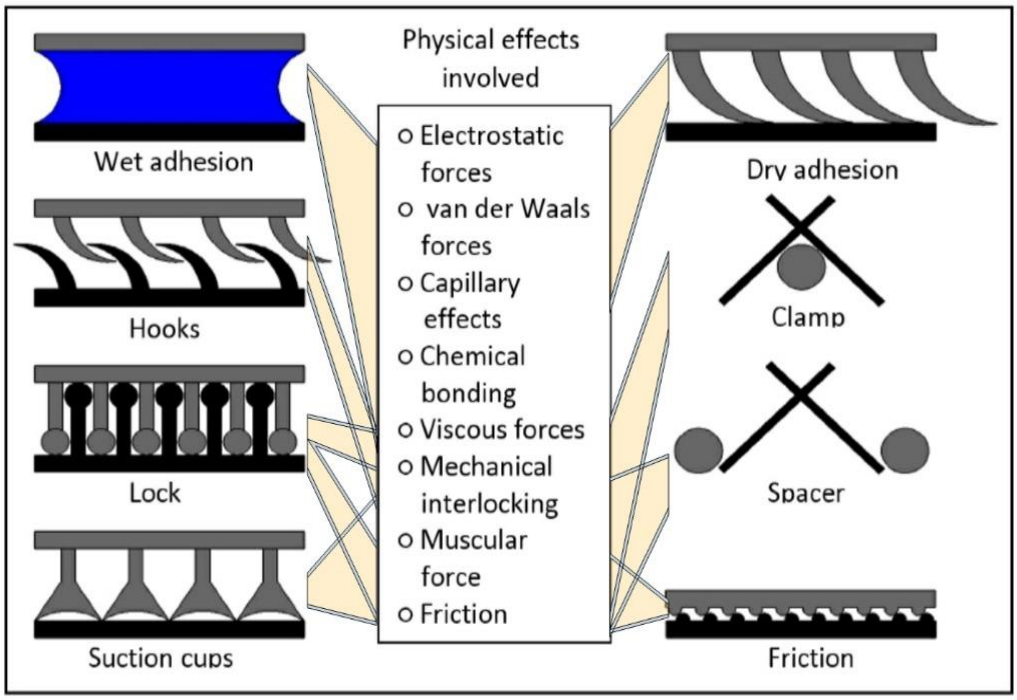


Figure 2.4 Schematic illustration biological mechanisms of attachment and physical effects involved [33].

2.3 Theories of Adhesion

There are six main theories of adhesion: physical adsorption, chemical bonding, diffusion, electrostatic, mechanical interlocking, and weak boundary layer. Although all adhesive bonds involve molecules in intimate contact, physical adsorption always contributes.

2.3.1 Physical Adsorption Theory

Physical adsorption is the most widely applicable theory of adhesion; as it contributes to all adhesive bonds [34]. The adsorption theory proposes that if there is

intimate contact between the substrate and the adhesive, interatomic and intermolecular forces will actuate across the surfaces interface, resulting in primary and secondary bonding. The most common of these bonding forces such forces are van der Waals forces and they can be sub-divided into three categories: dipole-dipole force, dipole-induced dipole force, and dispersion force between nonpolar molecules [35].

Table 2.6 van der Waals Interactions.

Van der Waals interactions	Dipole-dipole	Attractive force between two molecules, each having a permanent electric dipole moment.
	Dipole-induced dipole	Attractive force that results when a polar molecule with a permanent electric dipole moment, induce a dipole moment in a non-polar molecule.
	Dispersion Force	Attractive force that results between two non-polar molecules

When a solid surface involves van der Waals interactions, the total work of adhesion should be the sum of the following two components: van der Waals and acid-base interactions defined by:

$$W_A = W_A^L + W_A^{a-b} \quad (1)$$

where W_A is the total adhesion work, W_A^L is the van der Waals interaction, and W_A^{a-b} is the acid-base interaction.

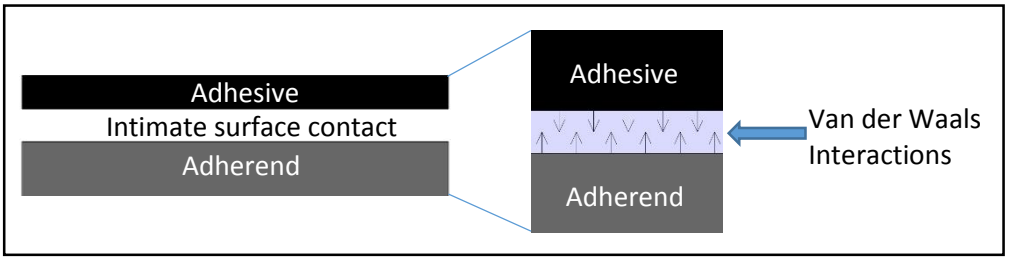


Figure 2.5 Schematic illustration of intimate contact and van der Waals interactions.

2.3.2 Chemical Bonding Theory

The chemical bonding theory attributes the formation of an adhesive bond between adhesive and adherent by chemical forces formed across the interface of the surfaces. This theory states that the formation of covalent, ionic or hydrogen bonds are the principal adhesion mechanism [36].

These bonds are generally considered as primary bonds in comparison with physical interactions, such as van der Waals, which are called secondary force interactions.

The terms primary and secondary stem from the relative strength or bond energy of each type of interaction. It is clear that the formation of chemical bonds depends on the reactivity between the surfaces [37].

Table 2.7 Typical strengths of chemical bonds and van der Waals interactions (kJ mol^{-1}) [36]

Chemical bonds		**Van der Waals interactions**	
Ionic			
$Na^{+}Cl^{-}$	503	Dipole-dipole	≥ 2
$Al^{3}O^{2-}$	4290	Dipole-induced dipole	0.05
$Ti^{4+}O^{2-}$	5340	Dispersion force	≥ 2
Covalent			
C-C	368		
C-O	377		
Si-O	368		
C-N	291		
Hydrogen Bond			
-OH▪▪▪OC=-	30 +/- 2		
-OH▪▪▪OH	32 +/- 6		
-OH▪▪▪N	35 +/- 2		
F^{-}▪▪▪HF	163 +/- 4		

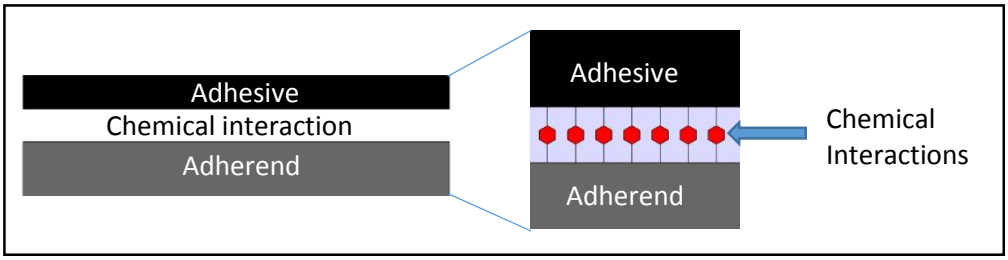


Figure 2.6 Schematic illustration of chemical interactions.

2.3.3 Diffusion Theory

The diffusion theory or (inter-diffusion) is based on the assumption that the adhesion strength of polymers is due to mutual inter-diffusion of macromolecules across the interface of surfaces creating an interphase.

The original interface area will become a multiphase interface which is composed of the mixture of the two materials. This implies that the macromolecular chains are mobile and mutually soluble [38].

Inter-diffusion is of great importance for scenarios such as healing and welding processes of polymers. Therefore, when inter-diffusion is involved, the bond strength should depend on different factors such as contact time, temperature, nature and molecular weight of the polymer [39].

Hildebrand has proposed [40] that the amount of energy necessary to take all of the atoms or molecules in a mole of material and separate them to an infinite distance is given by:

$$E_{coh} = \Delta H_{vap} - R\,T \quad (2)$$

where E_{coh}, is the cohesive energy of a given material, ΔH_{vap} is the enthalpy of vaporization, R is the gas constant, and T is the absolute temperature.

Hence, the cohesive energy density equation (CED) can be used to interpret diffusion bonding. Bond strength is maximized when solubility parameters are matched between the adhesive and adherend.

$$CED = \frac{E_{coh}}{V} \quad (3)$$

$$\delta = \sqrt{\frac{E_{coh}}{V}} \quad (4)$$

where CED is the cohesive energy density, V is the molar volume, and δ is the solubility parameter.

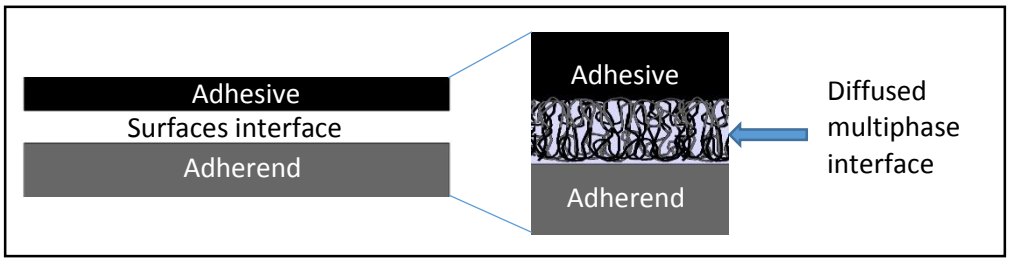


Figure 2.7 Schematic illustration of inter-diffusion between two surfaces.

2.3.4 Electrostatic Theory

This theory proposes that the formation of adhesive bonds between surfaces is due to electrostatic forces between the interface of the adhesive and adherent. At this interface, contact and transfer potentials are exhibited building up an electrical double layer, which gives a force of attraction between the two components [41].

The existence of electrochemical potential difference across the interface of the two materials in contact; will promote the movement of electrons or ions over the contact interface. This adhesion mechanism is considered distinct from any charge transfer [22].

Derjaguin has proposed [42] that for the electrostatic adhesion theory that Coulomb's law can be applied to calculate the electrostatic potential interaction between two particles separated to a certain distance in a dielectric medium through:

$$U^E = \frac{q_1 q_2}{\varepsilon r} \qquad (5)$$

where U^E is the electrostatic potential of interaction, $q_1 q_2$ are the particles charge, ε is the dielectric constant of the medium, and r is the distance between particles.

The magnitude of the adhesive force will depends on the number of charges per unit area and the distance of separation between charges, this can be calculated by the following expression:

$$W_A = 2\pi\sigma^2 H \qquad (6)$$

Where W_A is the work required to break the adhesive bond, σ is the surface charge density, and H is the distance of separation at the point of electrical break down.

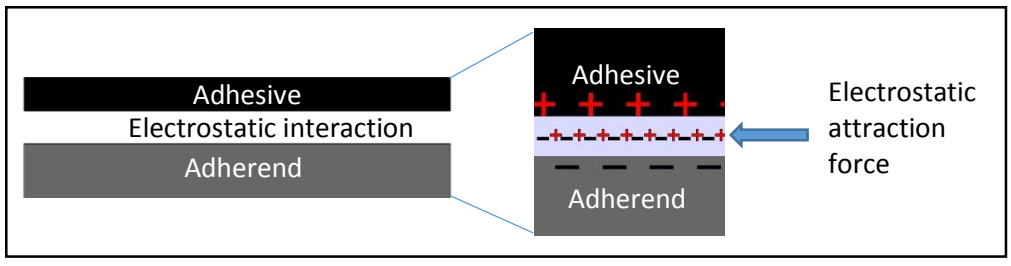


Figure 2.8 Schematic illustration of electrostatic forces between two surfaces.

2.3.5 Mechanical Interlocking Theory

Mechanical Interlocking Theory is based on the mechanical keying or interlocking of the adhesive into the cavities, pores, and surface asperities of the adherend. According to Macbain and Hopkins [43] this is the major factor determining the adhesive strength between the surfaces.

Basically, the adhesive flows to the morphological irregularities; displacing trapped air at the interface. Therefore, if the adhesive can penetrate into the surface roughness of the adherend, this can create a bond between the surfaces.

If wetting conditions allows the conformation of the adhesive into the pores and cavities, then the enhancement of adhesion by mechanical interlocking can be associated to the contact increase in the interfacial area due the surface roughness.

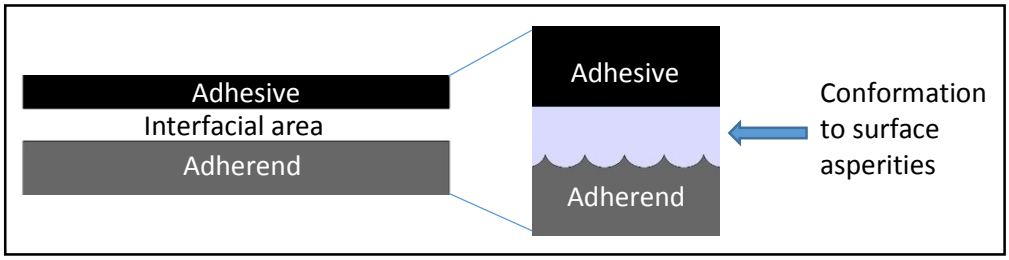


Figure 2.9 Schematic illustration of mechanical interlocking of the adhesive into surface asperities.

2.3.6 Weak Boundary Layer Theory

Weak Boundary Layer theory was proposed by J.J Bikerman [44]. It states that if an adhesive bond is made, the bond will fail in either the adherend or adhesive by a cohesive break or a weak boundary layer.

The bond will fail at less than their expected strength because of the existence of low cohesive strength at the interface. If impurities, such as rust, oils, particles or greases, are present near the bonding surface, a weak bond will be formed. The presence of low molecular weight compounds, such as antioxidants; and plasticizers, can form weak boundary layers.

2.4 Existing Synthetic Dry Adhesive Technologies

Bio-inspired adhesive materials are becoming of increase interest in different fields. In previous years, different researchers have worked towards the development of synthetic materials with specific properties that can duplicate dry adhesive mechanism found in the attachment pads of biological systems such as geckos, spiders, beetles, and bats.

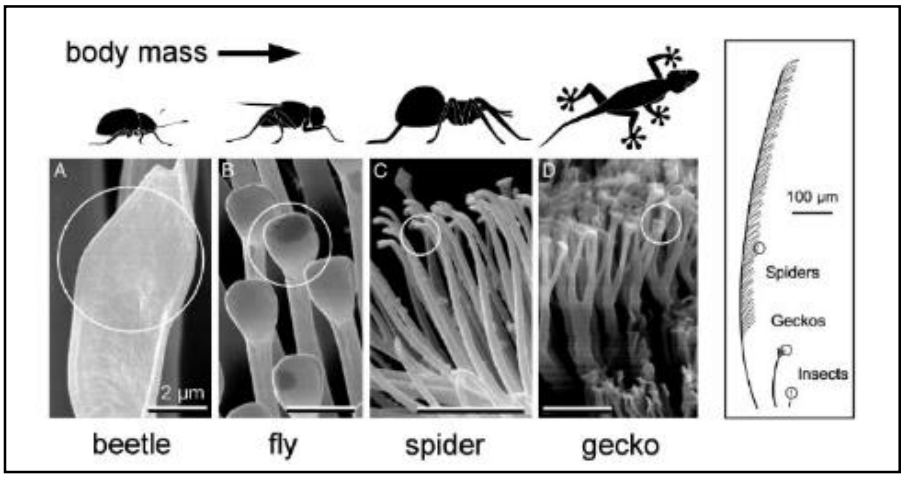


Figure 2.10 Terminal elements (circles) in animals with hairy design of attachment pads [45].

Based on the science behind the interaction of the attachment pads and substrates, researches have proposed different methods to produce reversible dry adhesive materials. The most commons being: micro-nano molding, nano-embossing, carbon nanotubes growth, and lithography.

2.4.1 Micro-nano Molding

Micro-nano molding is a method of forming micro and nano patterns in an elastomeric surface to create a forest of nanopillars. Micro-nano molding is based on the fibrillar structures of biological systems used as attachment mechanisms, with the purpose of replicate their adhesive pads properties.

Del Campo et al. [46] used a combination of soft-molding, and elastomeric precursors to pattern a master die for the creation of fibrillar arrays reporting measurements using the pull-off test with forces up to 25 mN.

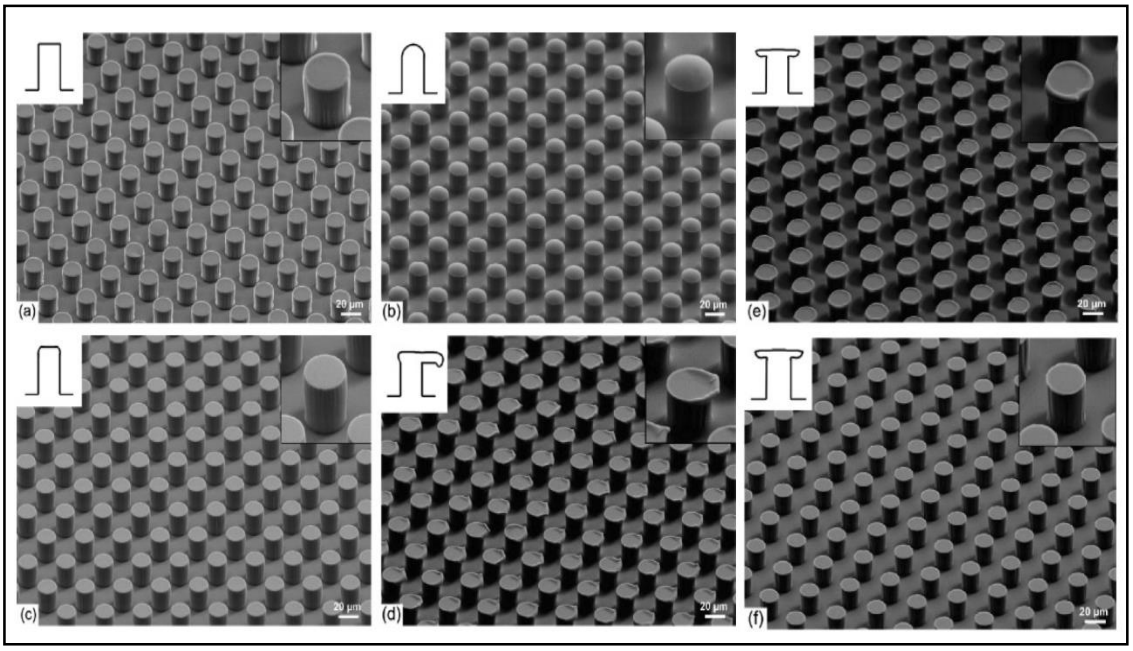


Figure 2.11 SEM images of selected patterns with different tip geometries: (a) Flat, (b) Spherical, (c) Flat with round edges, (d) Spatula, (e) Mushroom (ink/printed), (f) Mushroom (molded). Pillars have a radius of 10 μm and a height of about 20 μm [46].

Sitti and co-workers [47] proposed two different nanomolding techniques based on master templates with micro-nano geometries, both made under vacuum conditions

and on elastomeric materials: The first one is proposed the use of a nano-probe to indent a flat wax surface; the second one uses a patterned nano-probe membrane as a conforming template, obtaining values of adhesion force up to 300 nN.

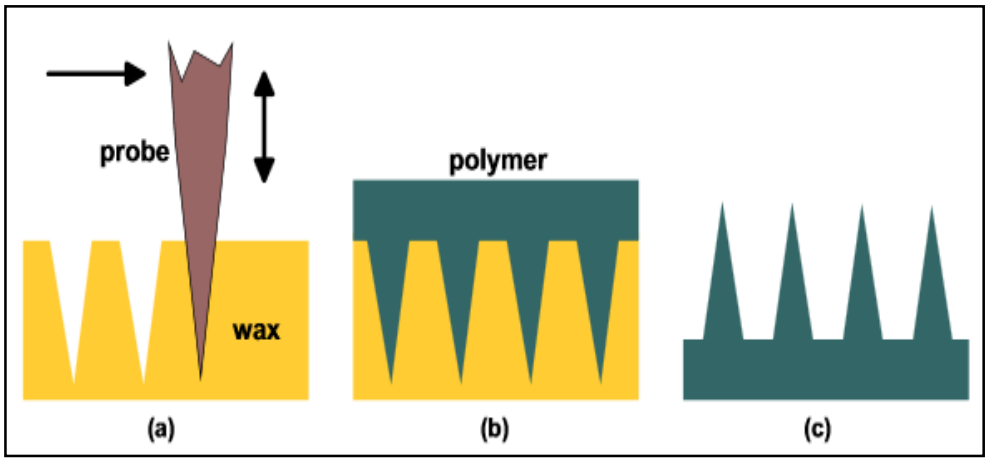


Figure 2.12 Synthetic hair fabrication by indentation of the mold: (a) Indenting a flat wax surface using a fabricated micro-nano tip, (b) Molding the polymer, (c) Molded polymer [47].

2.4.2 Nano Embossing

The Nano Embossing technique offers a broad variety of surface patterning. The development in the last years of this method have lead researches to the use of hot embossing lithography and UV to create high aspect ratios geometries by thermoplastic molding. Kim and co-workers [48] have proposed the creation of high aspect ratio

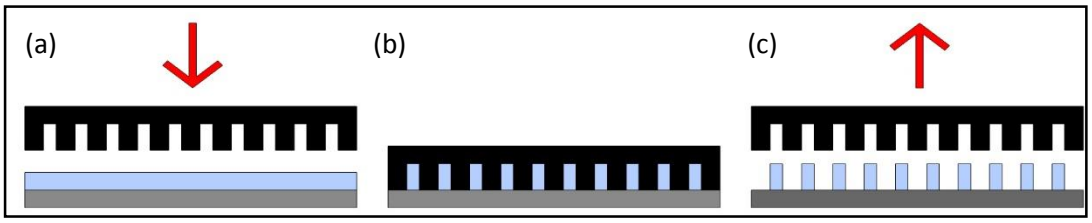


Figure 2.13 Schematic illustration of nano embossing process. (a) Loading specimen, (b) Embossing, (c) Unmold.

2.4.3 Carbon Nanotubes

Carbon nanotubes growth has been used to fabricate gecko inspired synthetic dry adhesives due to their high aspect ratio, modulus and high mechanical strength. Arrays of carbon nanotubes have been used by many researchers with the purpose of replicating the gecko's pad fibrillar structure.

Zhao et al. [49] using vertical aligned multiwalled carbon nanotube arrays reported adhesive strengths of 8 N/cm^2 in mode II and 10 N/cm^2 in mode I over a glass surface. Ge et al [50] reported a mode II adhesive strength of 36 N/cm^2 transferring micro patterned carbon nanotubes arrays onto a flexible polymer film.

Qu and co-workers [51] using vertically aligned multi-walled carbon nanotube arrays with a curly entangled tip reported values of shear adhesion force of 100 N/cm^2, and a normal adhesion force of 10 N/cm^2.

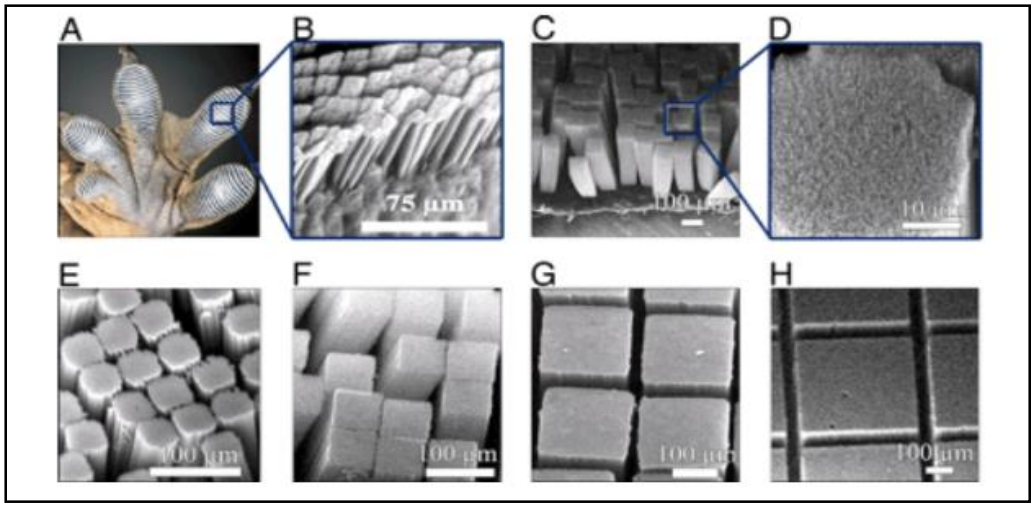


Figure 2.14 Microfabricated aligned multiwalled carbon nanotube setae and spatulas. (A) (A) Optical picture of gecko foot showing the setae. (B) SEM image of gecko setea. (C) Side view of synthetic MWCN setae. (D) Higher magnification view. (E-H) Synthetic MWCN setae of width 50 (E), 100(F), 200 (G), and 500 (H) μm [50].

2.4.4 Lithography

Lithography is another method used by researchers to produce surfaces with high aspect ratio shapes, forming fibrillar arrays of a desired configuration to mimic the nanostructure of geckos and other animals.

This process can be carried out by different conventional and unconventional methods. The most common being: atomic force microscope lithography [52], ultraviolet lithography [53], electron beam lithography (direct writing, induced deposition) [54, 55].

The indicated techniques essentially can be subdivided in two categories, defined on where the lithographic work is done. The first category is when the lithography is executed directly in the polymeric material to create the desired nano pattern and the second when the nano pattern is created in a master template.

Parness et al [56] have reported the fabrication of micro wedge-shaped arrays using micro molding and dual angle lithography with a shear strength of 17 kPa measured in a surface area of 1 cm^2.

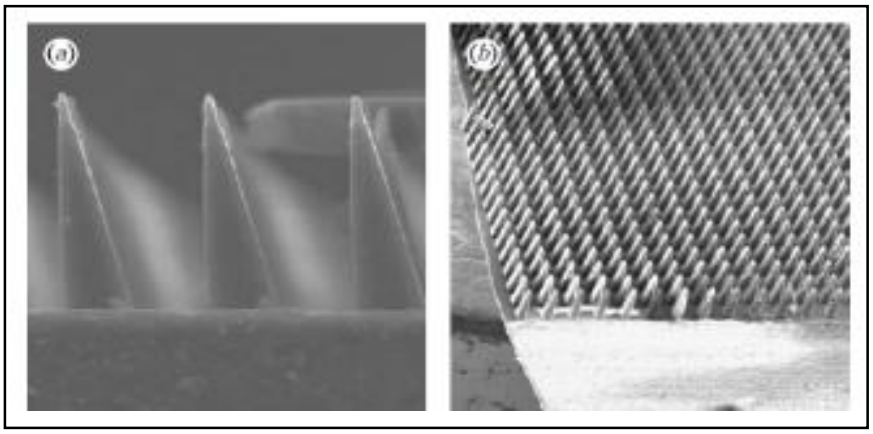


Figure 2.15 Scanning electron microscope images of microfabricated wedge-shaped adhesive arrays. (a) Side view of 20 μm base width by 80 μm height wedges. (b) Diagonal view of a large array of 50 μm base width by 200 μm height wedges.

2.5 Electrospinning Technique

Electrospinning is a process used to produce solid continuous fibers with diameters in the range of micro or nano scale from polymer solutions using electrostatic forces.

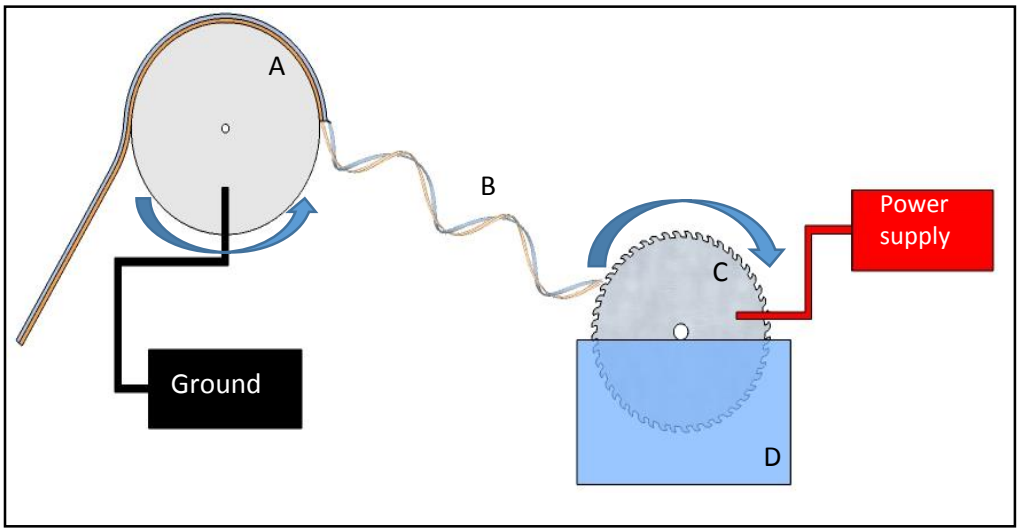


Figure 2.16 Schematic representation of Formhal's electrospinning set-up. (A) Grounded rotatory collector, (B) Polymer electrospun fibers, (C) Rotary spinner (positive charged), (D) Polymer solution bath.

In 1934, Anton Formhals patented an electrospinning device [57] His apparatus named "*Process and apparatus for preparing artificial threads*" was configured for the production of polymer filaments using electrostatic force, from there the term electrospinning.

One dimensional (1D) nanostructures, such as wires, rods, tubes and fibers, are of current interest among the scientific community. Since the 1990s, a number of advanced techniques have been developed to form this nanostructures including electron-beam, focused-ion-beam writing, lithography, hydrothermal, vapor deposition and electrospinning [58].

Among those methods, electrospinning is the simplest approach to fabricate 1D nano structures with solid and hollow interiors, continuous length, tunable diameter, aligned direction, controlled morphology and composition [59-61].

The singular advantages of electrospinning and the multi-functional properties of the produced fibers have made this a very suitable method to fabricate nano materials to be used in many applications: nano reinforcement, filtration systems, catalysis, electronics, and lithium-ion batteries.

Wong and co-workers introduced electrospinning and electrospun nanofibers into the adhesion field [8-15] reporting the adhesion strength between two free standing fibers

[8]. Subsequently, they produced arrays of electrospun nylon-6 nanofibers [12] which exhibit a high mode II shear adhesion of 27 N/cm^2.

There are 3 major parameters that controls the electrospinning process: Solution parameters, processing parameters and ambient parameters.

2.5.1 Solution Parameters

Solution parameters has a direct influence in the electrospun adhesive nanofibers surface morphology , their adhesive behavior, physical and mechanical properties.

2.5.1.1 Concentration

Concentration of polymer solution plays an important role in the fiber formation during the electrospinning process. Depending on this, fibers can be obtained or not.

If a polymer solution with low concentration is processed, no fibers will be obtained. Instead, nano or micro particles will be collected, and and electrospray will occur instead of electrospinning [62].

If the solution has a higher concentration a mixture of fibers and beads will be collected [63]. When the concentration is optimum, nanofibers can be obtained. If the concentration is very high, nanofibers will not be electrospun. Instead, helix-shaped micro ribbons will be observed [64].

Demir et al. [65] demonstrated that the fiber diameter increases with increasing polymer concentration according to a power law relationship [66].

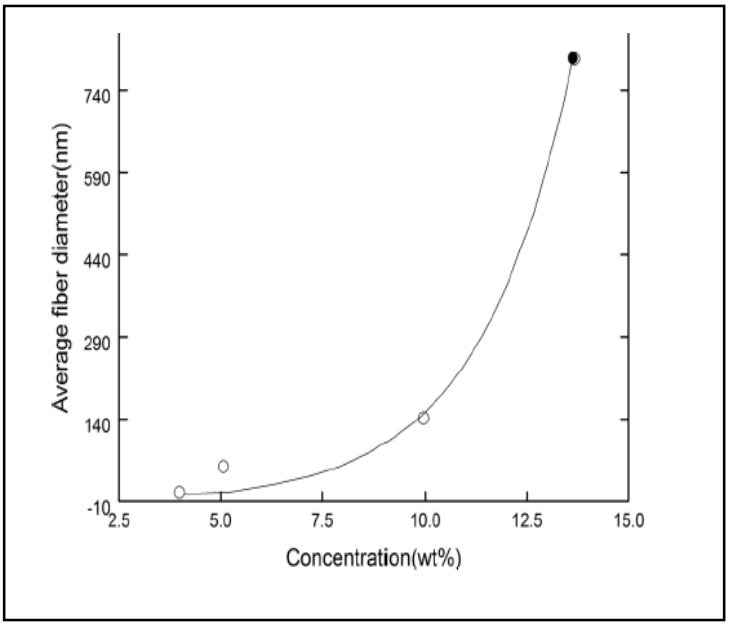


Figure 2.17 Average fiber diameter of polyurethane fibers, as function of concentration [66].

2.5.1.2 Molecular Weight

Morphology of the electrospun nanofibers is direct influenced by the molecular weight of the polymer used, this reflects the entanglement of polymer chains in solution, specially the solution viscosity.

In principle, molecular weight reflects the entanglement of polymer chains in solutions, namely the solution viscosity.

The appearance of beads will be more likely with lower molecular weight. However, higher molecular weight ensures the presence of smooth fibers [67].

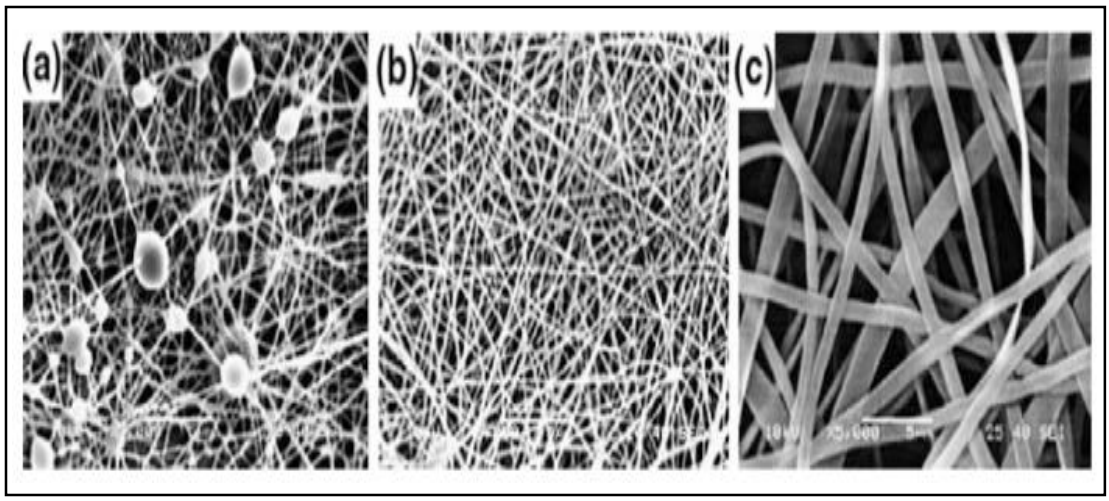


Figure 2.18 Electrospun polymer nanofibers morphology for various molecular weights. (a) 9,000-10,000 g/mol; (b) 13,000-23,000 g/mol; (c) 31,000-50,000 g/mol [67].

2.5.1.3 Viscosity

Solution viscosity is a determining factor in the nanofibers morphology, this can be tuned by adjusting the polymer concentration of the solution.

Viscosity and concentration of the solution are intimately related [68, 69]. Experimental findings show that the diameter of the electrospun fibers is dependent of concentration and polymer chain conformation in solution. This can be expressed in terms of Berry's number which is defined as the dimensionless product of the intrinsic viscosity of the solution and the concentration given as[70]:

$$B_e = [\eta] * C \quad (7)$$

where B_e is Berry's number, η is the intrinsic polymer viscosity and C is the polymer concentration.

2.5.1.4 Surface Tension

Surface tension is directly influenced by the solvent composition in solution. Koombhongse and co-workers [71] reported that different solvents may contribute different surface tensions.

The experiment was carried out by electrospinning a solution based on polystyrene (PS) in 18 different solvents, with a fixed concentration (10, 20, and 30 w/v), voltage and collection distance of 20 kV and 10 cm.

They successfully electrospun fibers from solutions with 1,2-dicloroethane, DMF, ethylacetate, MEK, and THF. The qualitative evaluation of the influence of solvent in the morphology of the electrospun fibers it is shown in figure 3.2.

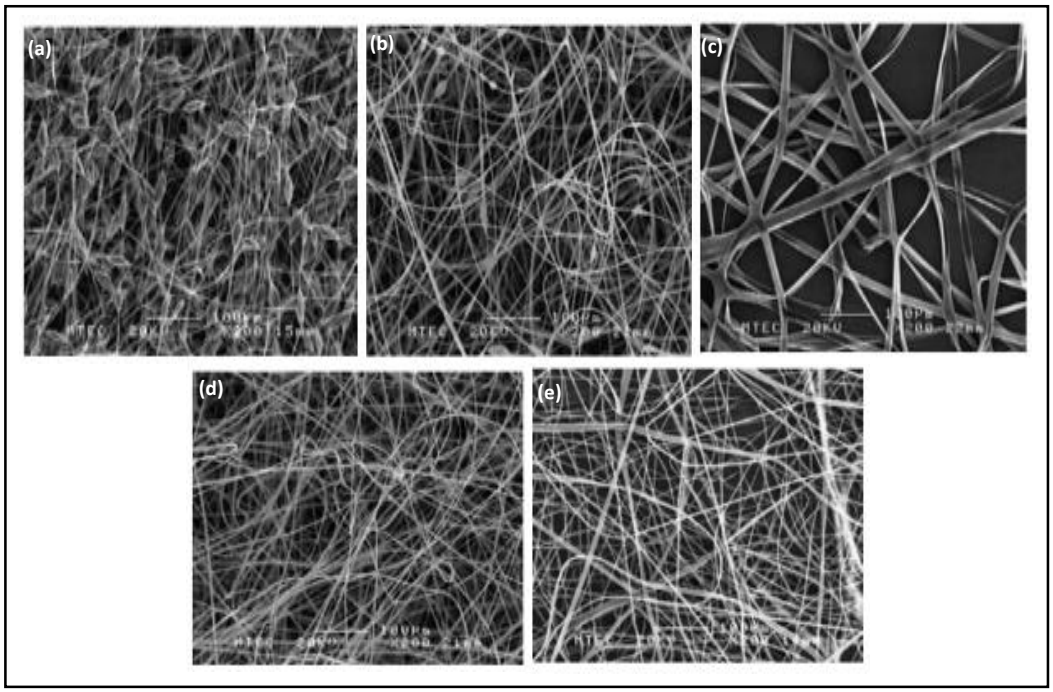


Figure 2.19 SEM micrographs of polystyrene electrospun fibers with fixed concentration of 20 % (w/v) on different solvents. (a) 1,2-Dichloroethane, (b) DMF, (c) Ethylacetate, (d) MEK, (e) THF [71].

2.5.1.5 Solution Conductivity

Solution conductivity is determined essentially by the solvent and polymer system used, depending on this a solution can or can't be electrospun.

Angammana et al. [72] reported the influence of solution conductivity on average fiber diameter of PEO electrospun nanofibers, improvement of electrical conductivity in the solution with the addition of ionic salts was reported by Jun et al. [69]. Huang et al. [73] reported a high increase of solution conductivity using formic acid.

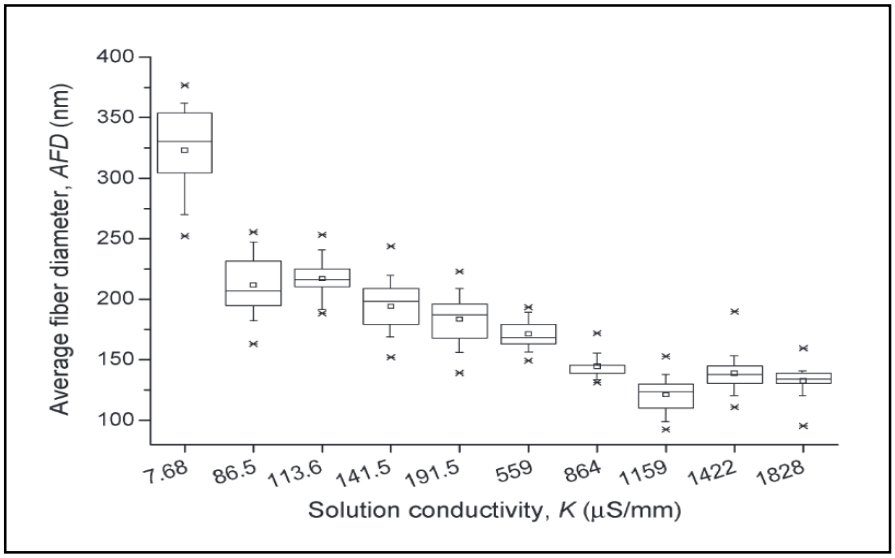


Figure 2.20 Variation in the average diameter of PEO electrospun nanofibers with the increase in solution conductivity using a fixed voltage and collecting distance, 15 kV and 200 mm respectively [72].

2.5.2 Processing Parameters

Processing parameters are the ones that are involved in the electrospinning process the most common: voltage, flow rate, collection method, and collection distance.

2.5.2.1 Voltage

Voltage is a crucial parameter in the electrospinning process. The whole electrostatic force that will originate the polymer jet ejection depends on the differential of potential between the collector and the pipet/spinner.

The required voltage to eject the charged polymer jets from the Taylor cone will vary depending on different parameters such as: polymer concentration-conductivity, solvent, and distance between the tip of the pipet/spinner and the collector. It has been proven that the fiber diameter and jet diameter [66] is directly influenced by the applied voltage.

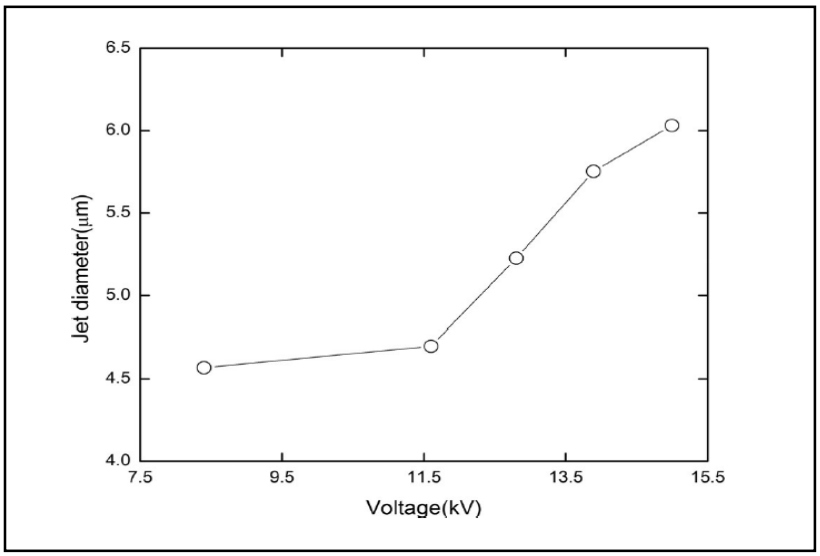


Figure 2.21 Nanofibers jet diameter as function of voltage applied [66].

2.5.2.2 Taylor Cone and Jet Formation

When voltage is applied, and the electric field reaches a critical value, the solution droplet at the tip of the needle overcomes its surface tension and starts a transition from the semi-circular shape to a cone shape, and from liquid to solid state. During this process, the droplet progressively deforms and becomes more and more elongated then the polymer jet is initiated [74].

In the 1960's Taylor [75, 76] did experimental research with electrically charged jets, and derived the condition for the critical electric potential needed to transform the droplet of liquid into a cone, proposing that the critical voltage is given by:

$$V_c^2 = 4\,\frac{H^2}{L^2}\left(\ln\frac{2L}{R} - \frac{3}{2}\right)(0.117\,\pi\gamma R) \qquad (8)$$

where V_c is the critical voltage, H is the distance between the capillary exit and the ground, L is the length of the capillary with radius R, and γ is the surface tension of the liquid.

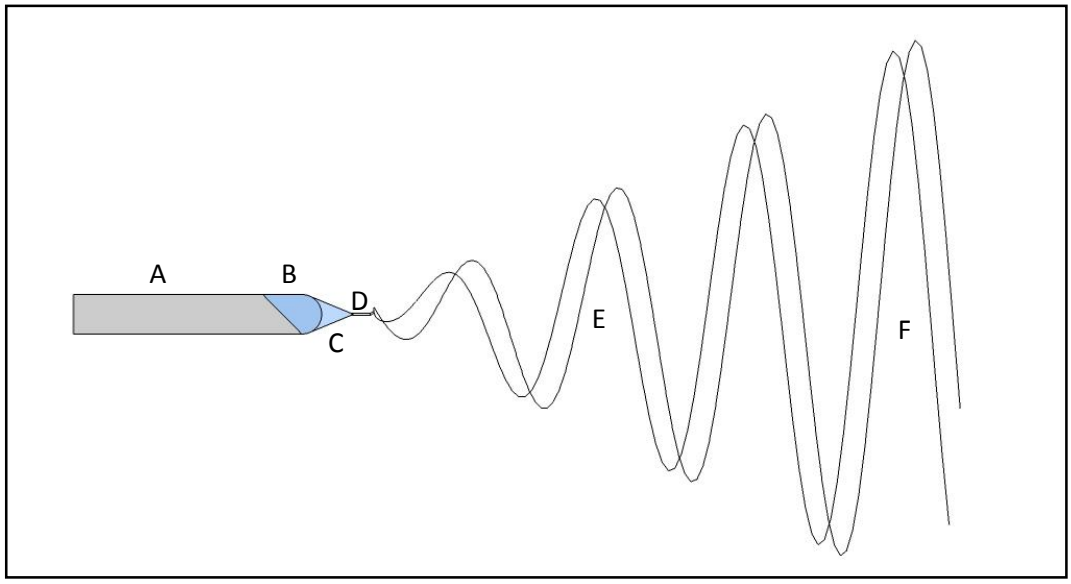


Figure 2.22 Different stages on electrospinning. (A) Needle tip, (B) Solution droplet, (C) Taylor cone, (D) Steady jet formation, (E) Instability of viscous jet, (F) Terminal state. The transition from liquid to solid occurs between points D and F.

Taylor also determined that the equilibrium between surface tension and electrostatic forces occurs when the half angle of the cone is 49.3° [76]. This value can be different for different polymer solutions. Rangkupan and Reneker et al. [77] reported an angle of 37.5 for molten PP.

2.5.2.3 Flow Rate

The flow rate of the polymer solution also plays another crucial role in the electrospinning process. If the solution flow is too high, bead, and fibers of thick diameter will occur. On the other hand, if the solution is to flow is to low clogging could occur. Yuan and co-workers [78] documented the influence of flow rate on electrospun nanofibers from a 20% PSF/DMAC solution with fixed parameters using flow rates of 0.40 and 0.66 ml/h respectively.

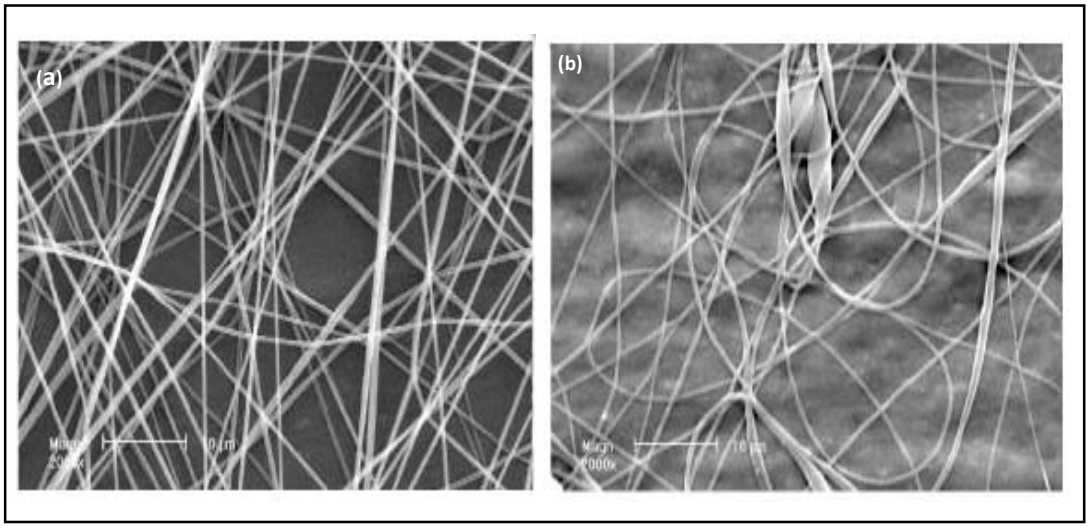


Figure 2.23 SEM micrographs of the effect of flow rate on the diameter of the PSF fibers (20% PSF/DMAC solution at 10kv). (a) 0.40 ml/h flow rate, (b) 0.66 ml/h flow rate [78].

2.5.2.4 Collectors

The utilized method for collecting the fibers during the electrospinning process has a crucial effect on the morphology and mechanical properties of the nanofibers array.

Different research groups have reported diverse collecting techniques the most common being: static collector, rotating drum, rotating disc, wired drum, independent electrodes, and pins.

The static collector or also called basic electrospinning setup, consist of a syringe or pipet with an electrified needle and a planar conductive grounded collector in which the fibers depositi in a random fashion.

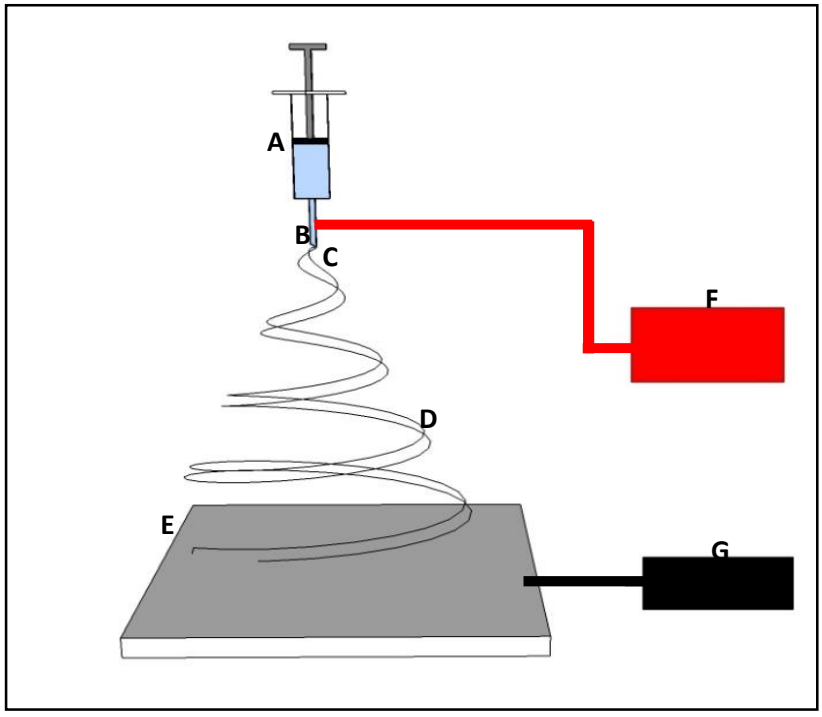


Figure 2.24 Static collector (basic electrospinning set-up. (A) Syringe filled with polymer solution, (B) Needle, (C) Taylor cone, (D) Instability of viscous jet, (E) Terminal state, (F) High voltage power supply, (G) Ground.

Wong and co-workers have reported the use of rotating disc [8,10,12], and parallel electrodes [8]. Rotating roller collector also have also been reported for the collection of electrospun nanofibers. These collection methods allow to control the deposition and the grade of alignment of the nano fibers.

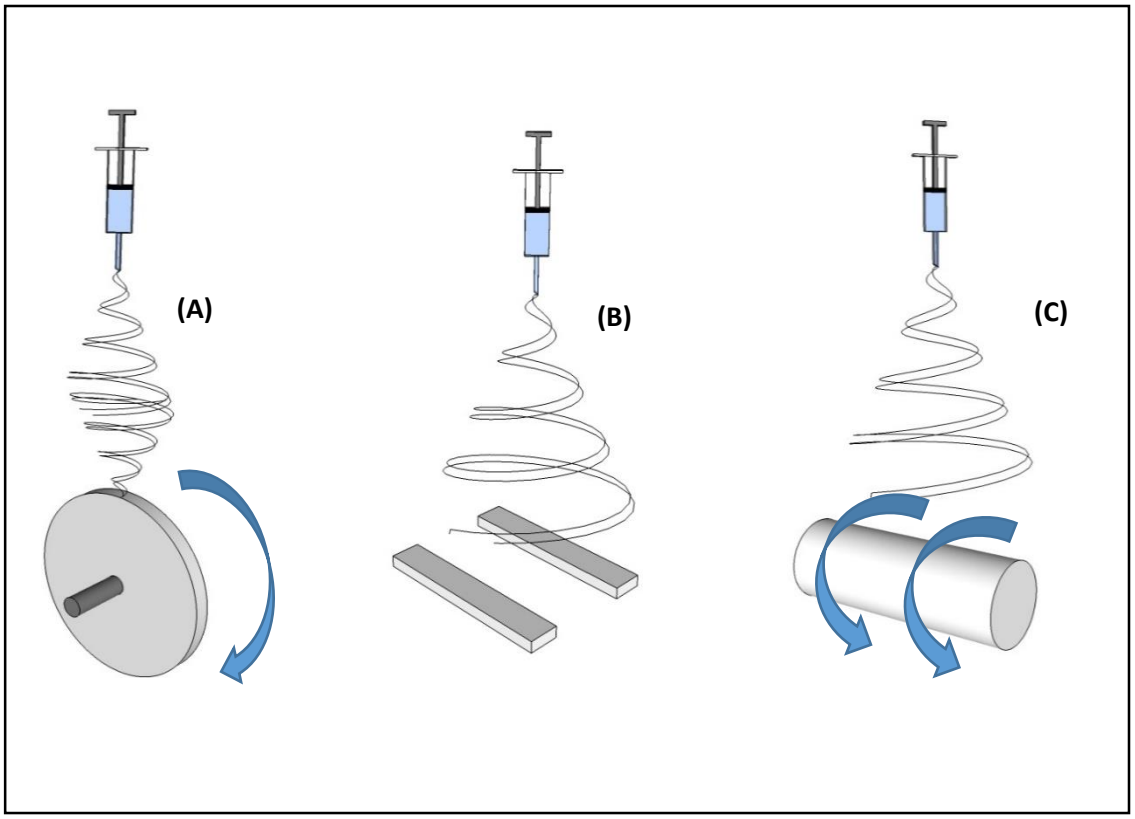


Figure 2.25 Electrospinning collection methods. (A) Rotating disk, (B) Parallel electrodes, (C) Rotating roller. Collectors must be grounded and syringe possitive charged.

Chase et al. [79] has reported the use of a wired rotating drum to collect and align the nano fibers. This setup consists in a set of plexiglass disks with a net of copper wires parallel to the axis of rotation with a separation between wires of 1cm.

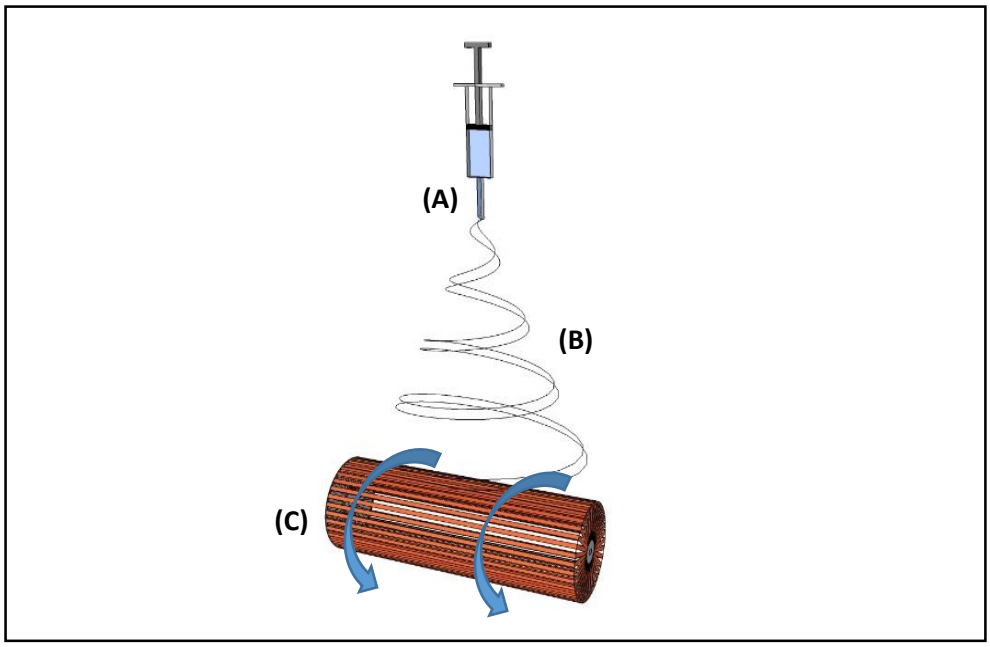


Figure 2.26 Wired rotating drum. (A) Syringe needle, (B) Polymer Jet, (C) Wired rotating drum.

Sundaray et al. [80] has reported the use of a thin, stainless steel pin with a sharp tip as a collector, mounted vertically so that the tip of the pin lies exactly below the syringe needle.

The polymer solution was filled in the syringe with a fine wire inserted as an electrode. The steel pin was aligned with the needle tip and is used as the grounded electrode. A 1 mm thick flexible plastic film was wrapped around the insulating cylinder attached to the motor M2 and used as substrate.

Motor M1 serves as a step motor to move motor M2 and substrate as a lead screw arrangement over the grounded stainless steel tip.

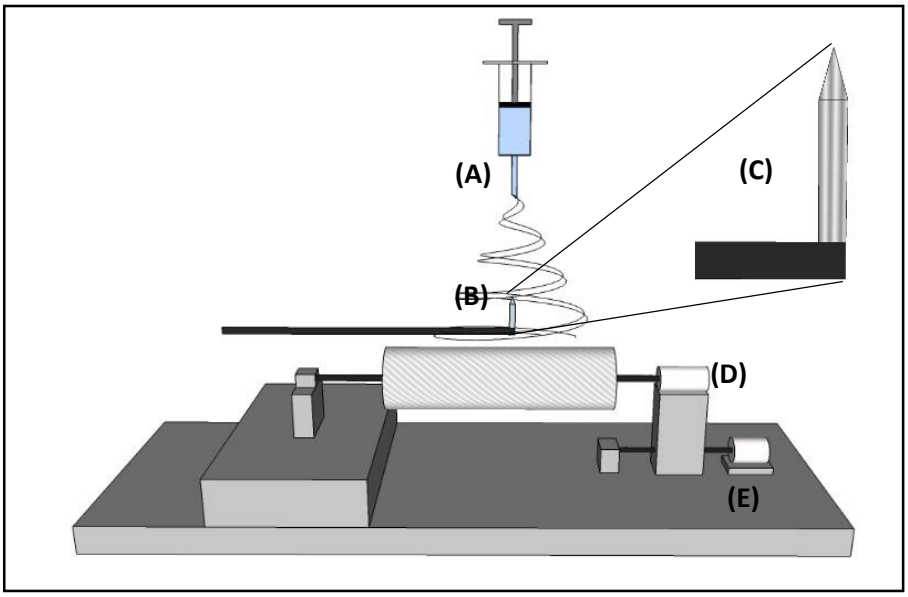


Figure 2.27 Electrospinning process using a stainless steel pin as collector. (A) Syringe needle, (B) Stainless steel pin, (C) Zoom view of pin, (D) Motor M2, (E)Motor M1.

2.5.2.5 Collection distance

The distance between the collector and the tip of the needle directly affects the fiber morphology and diameter. If the distance is too short, the fiber will not have enough time to solidify before reaching the collector. If the distance is too long, beads fiber can be formed and the electric field force can be reduced.

Yuan et al. [78] demonstrated that with the increase of the separation distance, the reduction of fiber diameter is favored.

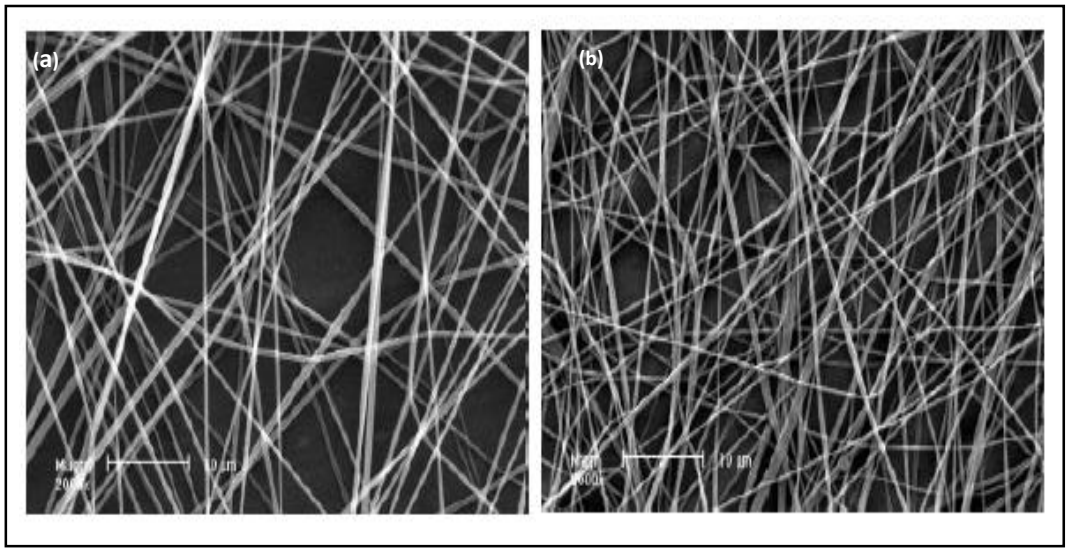


Figure 2.28 SEM micrographs of electrospun PSF fibers. Solution prepared at 20% PSF/DMAC, applied voltage of 10kV. Flow rate 0.40 ml/h. Collecting distance (a) 10 cm and (b) 15 cm. [78].

2.5.3 Ambient Parameters

Environmental parameters also affect the electrospinning process, nanofiber diameter and morphologies such as humidity and temperature. Mit-uppatham et al. [81] reported it by electrospinning a solution of polyamide-6 (PA 6-32) in 85% v/v formic acid in a concentration of 20% w/v.

They controlled the solution temperature using warm water with temperatures of 30, 40, 50, and 60°C for the electrospinning process. It was found that the electrospun fibers from the solution with a temperature of 60°C had a smaller diameter than the ones electrospun from the solutions at other temperatures. For every 10°C increased in the solution temperature, it was reported a reduction of approximately 4.32 % on diameter.

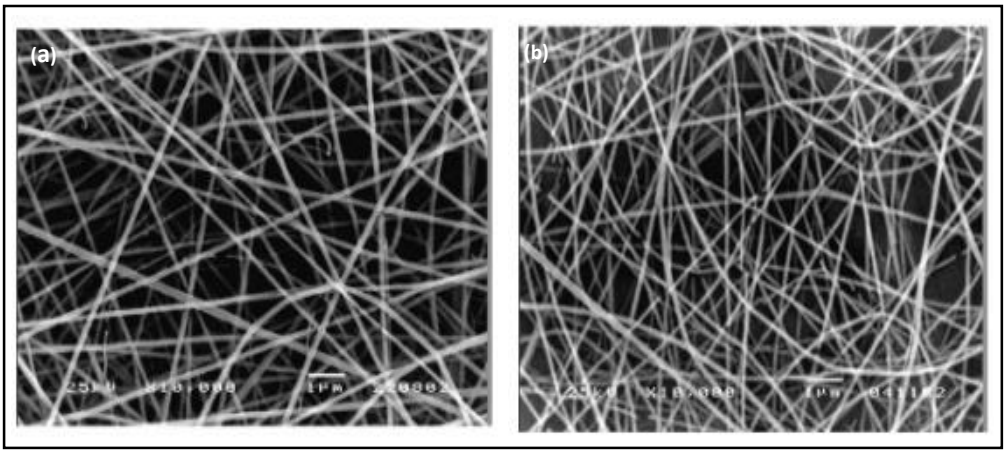
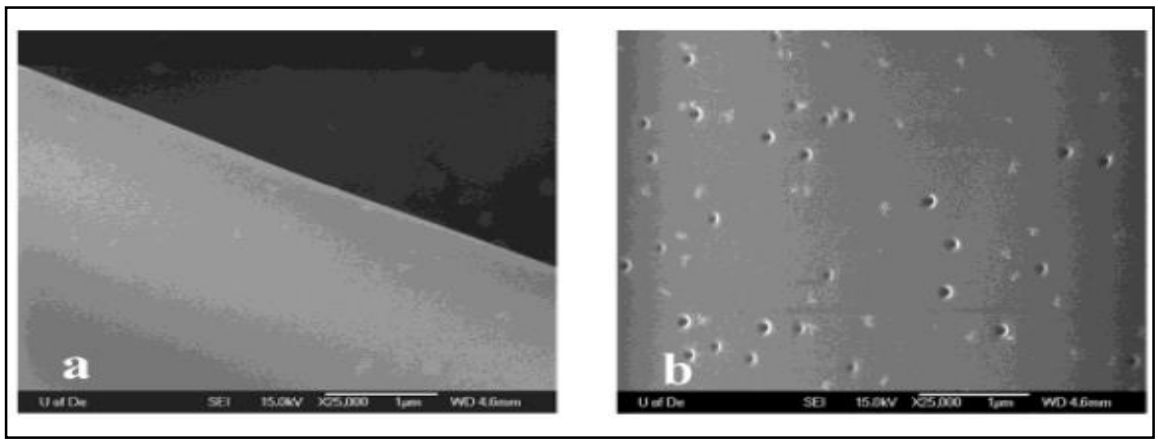


Figure 2.29 SEM micrograph of polyamide-6, (M_w=32,000 Da) at a concentration of 20% w/v in 85% v/v formic acid at solution temperatures of (a) 30°C and (b) 60 °C. Reported fiber diameter 89.7 +/- 5.6 and 98.3 +/- 8.2 nanometers for (a) and (b) respectively [81].

Humidity also affects both the process and the fibers. If low humidity may increase the solvent evaporation rate, on the contrary high humidity will lead to thicker fiber diameter due that the charge on the jet is neutralized and the stretching force become small. It has been demonstrated that humidity can also affect the surface morphology of the nanofibers [82].



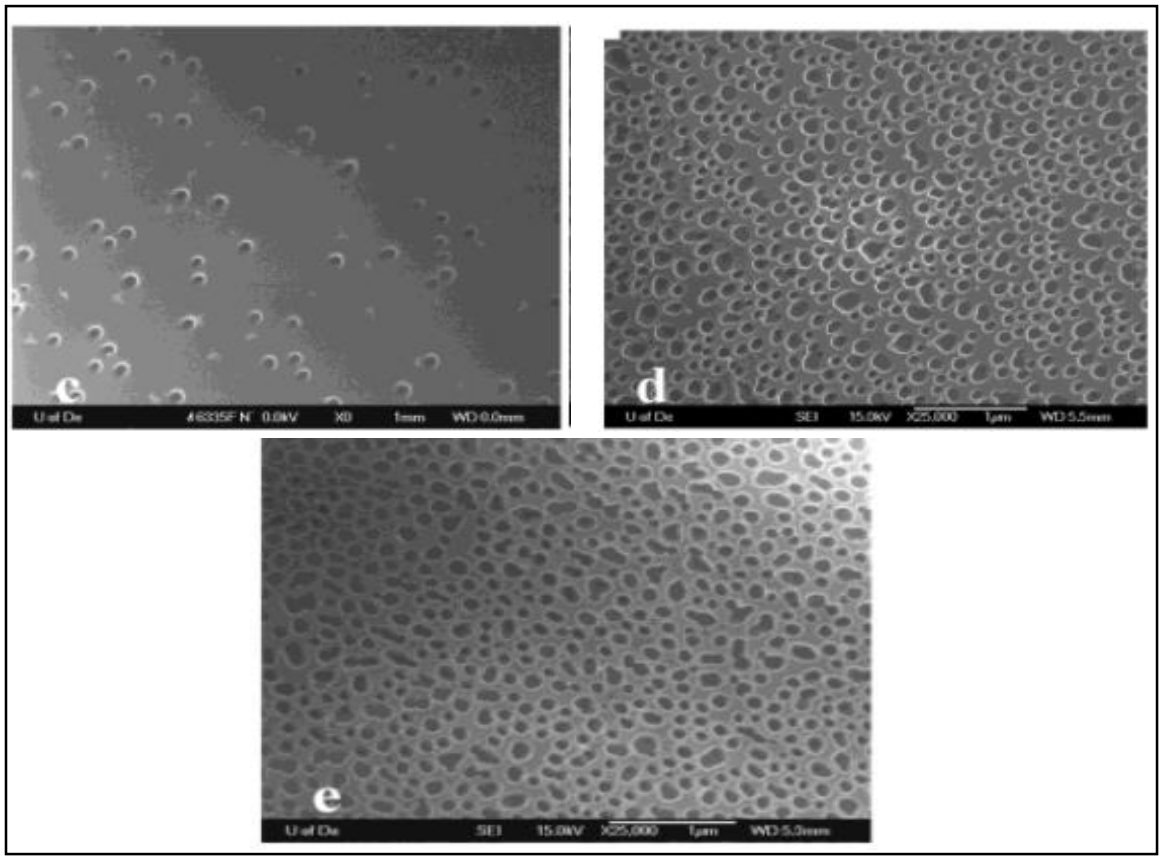


Figure 2.30 SEM micrograph of PS/THF electrospun fibers under varying humidity. (a) < 25%, (b) 31-38%, (c) 40-45%, (d) 50-59%, (e) 60-75% [82].

2.6 Interfacial Contact

The contact between two surfaces is named interfacial contact, it is very important for the adhesive flow the surface energy and substrate contact angle.

2.6.1 Surface Energy

Surface energy is directly associated with the formation of adhesive bonds, the strength of attraction between two surfaces or two molecules is determined by the surface energy of the materials. The higher the surface energy, the greater molecular attraction

will be exhibited. The lower the surface energy the attraction force between molecules will be reduced.

For an optimum adhesive bond, the adhesive material must intimately wet the surface of the adherend; this means that the adhesive material must flow and cover completely the surface of the adherend to maximize the contact area.

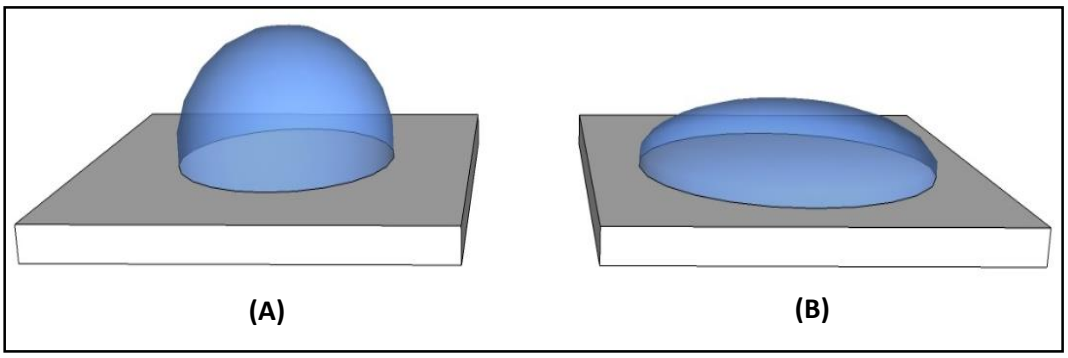


Figure 2.31 Schematic representation of effect of surface energy. (A) Low surface energy, (B) High surface energy.

2.6.2 Wetting

The good conformability of the adhesive to the adherent surface or "wetting" is a requisite to obtain a good adhesive bond. Wetting can be defined as the spreading of a liquid over a solid surface Wwhen a sufficiently intimate contact between the two phases is achieved, the inter-molecular forces will cause the conformability of the flowing phase into the surface asperities of the solid phase in a macro and micro scale.

The specific wettability of a solid can be defined using the measure of the contact angle, and the tension at the three phases contact point. This was proposed by Young [84] in the well-known Young's equation.

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \, COS \, \theta \quad (9)$$

Where γ_{SV}, γ_{LV}, γ_{SL} represents respectively the interfacial energies of the solid-vapor, solid-liquid, and liquid-vapor interfaces, θ represents the contact angle of the liquid.

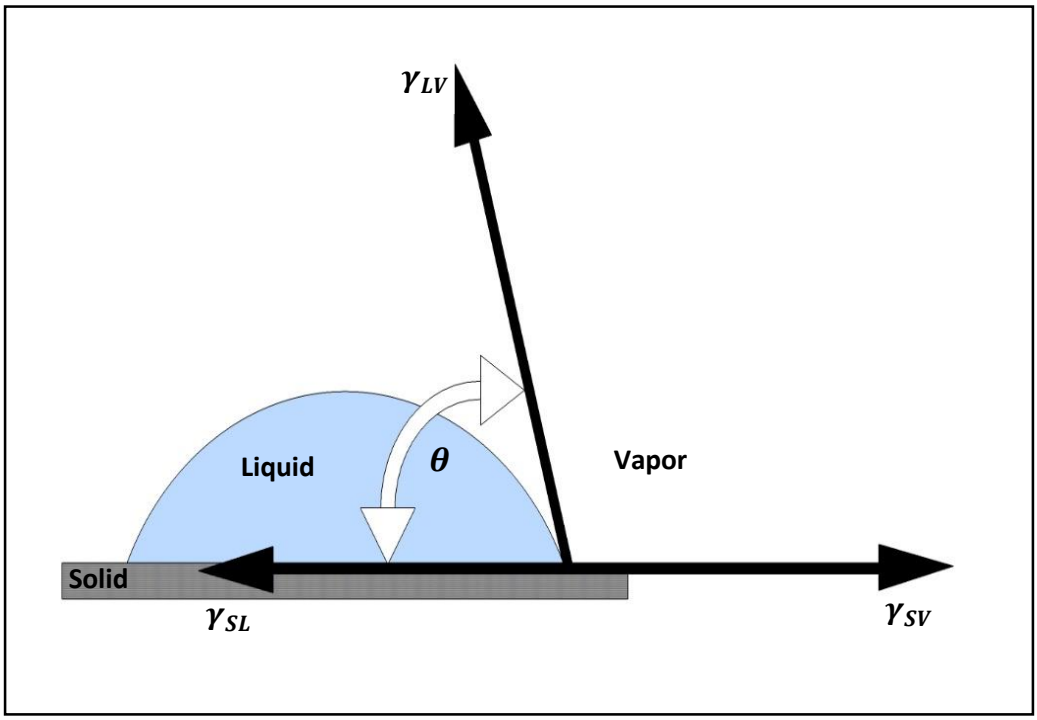


Figure 2.32 A liquid droplet resting at equilibrium on a solid surface.

2.6.3 Contact Angle

Contact angle is the angle that a liquid creates at the interface of the liquid/vapor with the solid phase, and it's the quantitative measure of wetting of a solid by a liquid

To measure how well a liquid wets a given surface, a droplet of the liquid is deposited on the surface and observed.

The angle from the solid/liquid interface to the tangent of the outline of the liquid/vapor interface is measured and this value is the contact angle for that specific system. The tendency of how a liquid spreads on a solid surface is characterized by the contact angle.

The boundary between wetting and non-wetting conditions is generally taken as $\theta = 90°$. For$\theta < 90°$, wetting occurs, and this is called a hydrophilic surface, while $\theta > 90°$ represent a condition of non-wetting also called a hydrophobic surface. When $\theta < 5°$ the surface is called a super hydrophilic and when the value of θ is largere than 150° is named superhydrophobic [85].

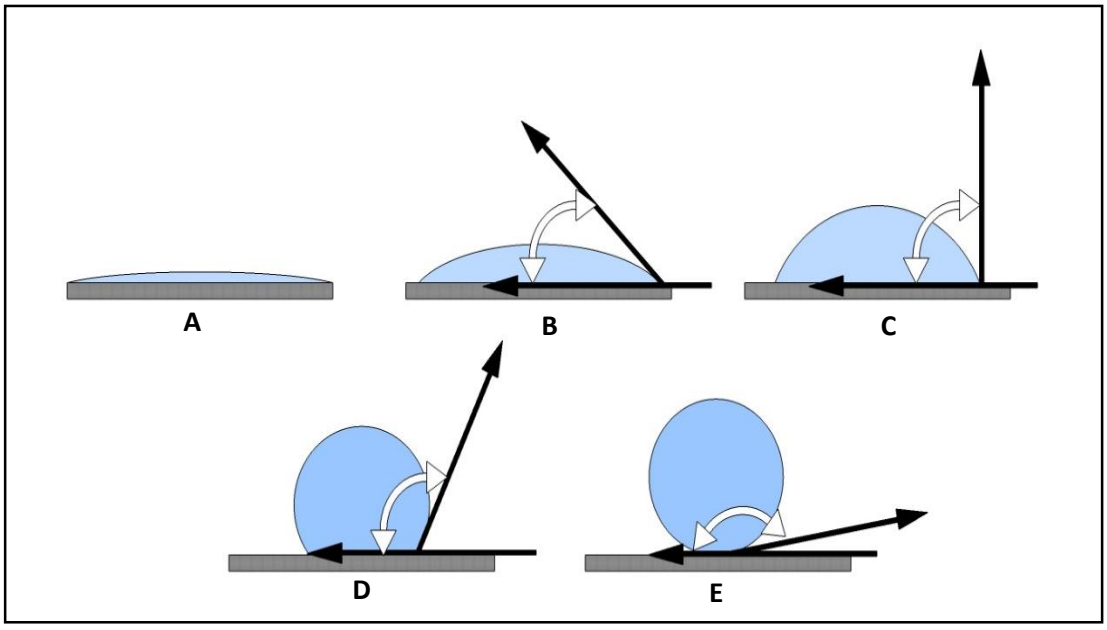


Figure 2.33 Contact angle and wetting behavior for a droplet on a solid surface. (A) Superhydrophillic behavior, contact angle $\theta < 5°$, (B) Hydrophillic behavior, contact

angle $\theta < 90°$, (C) Wetting / non-wetting boundary $\theta = 90°$, (D) Hydrophobic behavior, contact angle $\theta > 90°$, (E) Superhydrophobic behavior, contact angle $\theta > 150°$ [85].

2.7 Peeling Test

Adhesive strength is measured for many different purposes. Peel testing is one way to characterize adhesive bonds evaluating the resistance to highly localized stresses generally used on flexible tapes and films.

A typical peel test can be performed in two ways: having two flexible adherends bonded to each other, and having a flexible adherend bonded to a solid substrate, the adhesive itself generally will be in the form of a thin film.

The peel adhesion, or peel strength, is a very important consideration for adhesive applications. If the final use of the adhesive is temporal (removable adhesives), the peel adhesion needs to preserve an optimal balance between a proper adhesion permitting an easy removal process or clean peel. On the other hand, if the application is a permanent adhesion, the peel strength must be maximized to guarantee a stable bond.

Normally the goal of the peel test is to determine the adhesive strength between the adherend and adhesive. This is measured using the average load per unit width required to delaminate one surface from the other. Different methods has been proposed to perform this test the most commons being: 90° peel , 180° peel, T- peel, climbing drum, and floating roller peel test.

2.7.1 90° and 180° Peel Test.

90° and 180° peel tests are designed to measure the peeling strength between a flexible film and rigid substrate. For this case, the rigid adherend can be aluminum, steel or fiber reinforced plastic composite. The flexible adherend can be either a thin aluminum or steel sheet, bonded to the adherend by a layer or adhesive film.

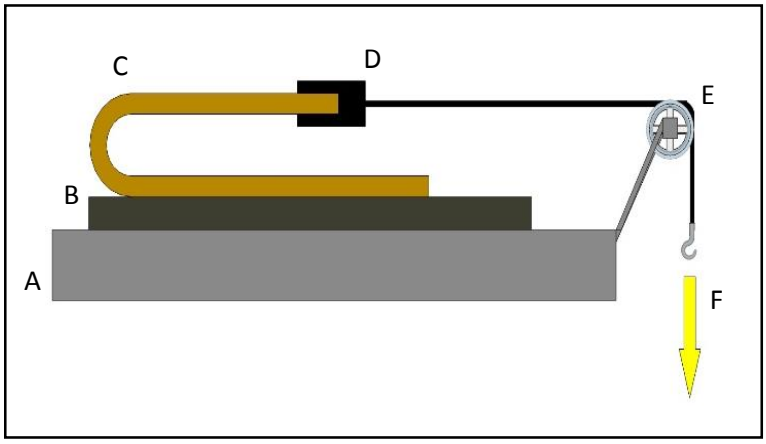


Figure 2.34 Schematic representation 180° degrees peeling test. (A) Support, (B) Rigid substrate, (C) Adhesive film, (D) Clamp, (E) Pulley, (F) Weight.

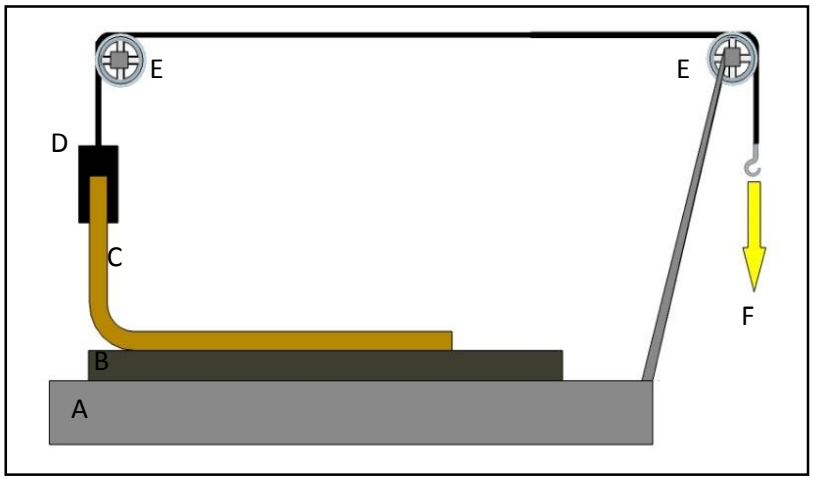


Figure 2.35 Schematic representation 90° degrees peeling test. (A) Support, (B) Rigid substrate, (C) Adhesive film, (D) Clamp, (E) Pulley, (F) Weight.

2.7.2 T- Peel Test

The T- peel test involves large adhesives deflections. Two relative flexible adherends are bonded together and then pulled apart with a 90° angle direction. If the adherend stifnesses are similar, the symmetric shape of the test configuration resembles a T, hence the name.

In this test, the adherends generally are thin, so the test can be performed with a relatively small amount of adhesive material. The induced loading may correspond to the actual peeling action required, as of a film away from a backing sheet.

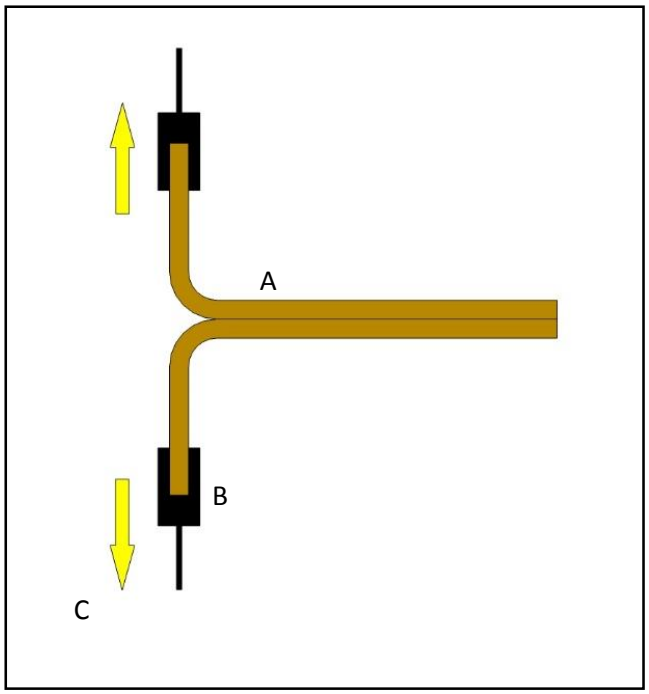


Figure 2.36 Schematic representation T-peel test. (A) Adhesive material, (B) Clamp, (C) Weight.

2.8 Adhesives on Industry

The use of adhesive materials can be vastly found in almost all industries, and manufacturing processes of the 21st century. Historically, fastening and joining techniques involved nails, rivets and bolts; with adhesive bonding limited just to the use of natural glues for wood working, paper, book binding and packaging.

The development of synthetic polymers in the 20th century, has boost the bond strength in adhesives. Technologies such as melamine, epoxy, polyester acrylate, methacrylate, and polyurethane became widely available for adhesives formulations.

Nowadays, adhesives in industry are being used to obtain a strong light weight bonds, between similar or dissimilar substrates; the ones requires high structural stability, strength in a diverse load and service life.

Special requirements in applications related to aerospace, automotive, and electronics has been fulfilled by joining methods based on adhesives. This adhesive joining technique involves glues, epoxies or various polymeric agents.

The use of adhesives offers many advantages during joining processes: stress loads distribution over bigger areas, high resistance to flexion and vibrations in joints, dissimilar materials with rough surfaces can be easily joined and the amount of weight increased to the system by the adhesive bond is almost negligible.

Some of the most representative industries involving adhesives in their manufacturing processes are:

- Transportation
- Building and construction
- Medical
- Assembly operations
- Electronics
- Consumer DIY
- Packaging
- Tape & label

2.8.1 Transportation

The transportation industry it is very extensive in terms of including the use of adhesives to their processes, among the most representative areas are: aerospace-aircraft, and automotive.

2.8.1.1 Automotive

Adhesive bonding is a universal technology that allows the joining of different materials giving advantages such as light weight design, and the mix of several different materials.

This has become increasingly important for the automotive industry, which is one of the most active industries in using adhesives. A large variety of applications can be found in the automotive production.

At least 25 different types of adhesives are utilized in the assembly of cars. The typical vehicle contains about 40 pounds of adhesives, about two-thirds of that goes into structural applications, the other third can goes into internal and external holding adhesives, and sealants [86].

Automotive adhesives must meet a number of requirements which are independent of join performance. They must be deliver good usability under specific conditions on the manufacturing process such as: minimal surface cleaning prior application, fast curing times, stand variable pressure and temperature.

Table 2.8 Common automotive adhesive application.

Use	Function	Type
Body and roof reinforcement panels	Structural	Vinyl plastisol
Double shell roof	Structural	Vinyl plastisol
Hood inner and outer panles	Structural	Vinyl plastisol
Brake shoes	Structural	Nitrile-phenolic
Door panel (interior)	Holding	Epoxy spray
Wiring harness clips (interior)	Holding	Vinyl plastisol
Ceiling fabric (interior)	Holding	Solvent cement
Body side molding (exterior)	Holding	Acrylate pressure sensitive
Stripping decals (exterior)	Holding	Acrylate pressure sensitive
Body sealers	Sealing	Bituminous
Gaskets	Sealing	Epoxy silicones

Adhesive welding	Sealing	Thermoplastic, heat expandable

2.8.1.1.1 Type of Failure

For adhesives in the automotive industry the type of failure that other adhesive bonds experience also apply to them: failure of one of the substrates, and failure of the adhesive.

When designing a bonded joint, is desired to achieve that the failure is within the adhesive. This will guarantee that the adhesion between the substrate and the adhesive material is higher than the cohesion of it, this will probe the full use of the adhesive. If the failure is in one of the substrates, the adhesive strength of the bond it is considerable less of what is expected.

In most cases failure occurs within the adhesion zone, this raises doubts when using adhesives in structural applications. When metallic substrates are bonded the failure mechanism could be due to the deterioration or corrosion of the layer of material that is in contact with the adhesion zone [87].

For plastic substrates, moisture plays a less important role. Plasticizer migration, residues of release agents, are often reasons for failure. When bonding sheet molding compounds or carbon fiber composites, moisture will have the same plasticizing effect on the matrix resin as on the adhesive, for this previous cases the weak boundary layer theory discussed on 2.3.6 can be applied.

2.8.1.2 Aerospace-aircraft

Adhesives are used extensively by the aerospace industry for bonding structural parts. Hot melts, and pressure sensitive adhesives are utilized in aircraft interiors; thermosetting adhesives and epoxies are used to bond load bearing structural components.

This industry also takes advantage of the lighter weight of the adhesive bonds over mechanical fastening, and their improved resistance to fatigue, elimination of stress concentration at the attachment points in mechanical fastening, redistribution of the stresses in wider areas. These attributes are critical to the aerospace industry and some of the most representative reasons for the extensively use of adhesives [88].

Adhesives for this industry have to be able to resist extreme changes on temperature, cyclic loads and creep.

Table 2.9 Most common adhesives in aircrafts.

Use	Function	Type
Bond metal sheets	Structural	Vinyl-phenolic
High temperature applications	Structural	Epoxi-phenolic
Sheet to sheet bonding	Structural	Nitrile-phenolic
Honeycomb sandwich	Structural	Nitrile-phenolic, epoxies
Hot temperature areas in engines	Structural	Polyimides
Interior fabric bonding	Holding	Rubber adhesive
Interior panel bonding	Holding	Phenolic resin
Sealing aircraft floors	Sealing	Polyurethane elastomer

One of the most common example of the use of adhesives in the aircraft structure is the joining process of the honeycomb sandwich composite, which is one of the principal structural component of the aircraft composed by: aluminum alloy faces, adhesive film and the honeycomb shape panel. The selection of the adhesive film need to comply with all the thermo-mechanical requirements for the aerospace industry.

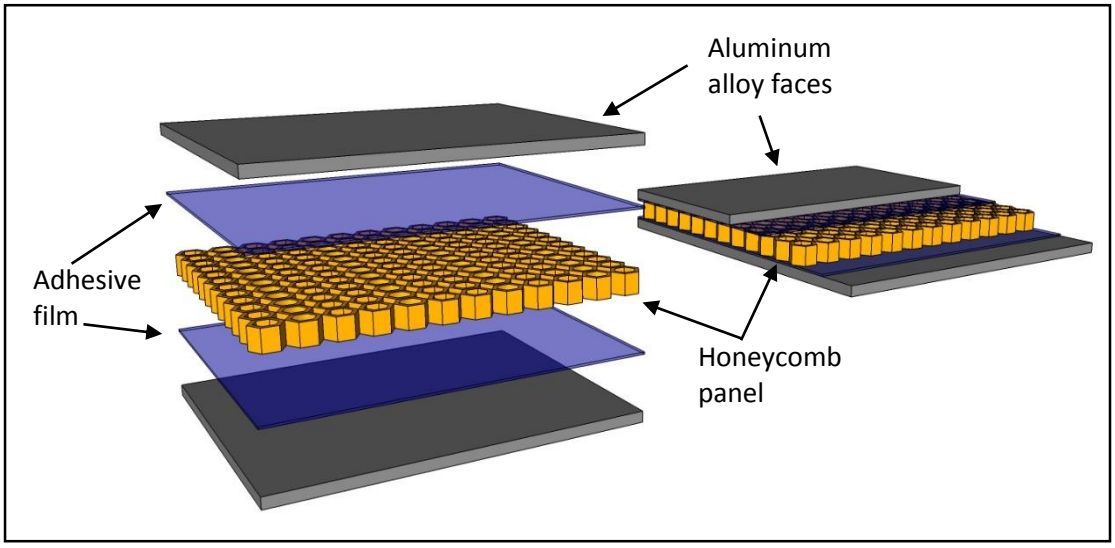


Figure 2.37 Honeycomb composite.

2.8.1.2.1 Type of Failure

Adhesives are used in bonding and sealing of critical aircraft structures such as fuselage and fuel tanks, but also in all the interior applications such as tray tables, seats, etc. There is a large repair industry for many of these components. The adhesives are required to be self-extinguishing.

For this industry very rigorous high safety margins must be met, to guarantee the durability of the and good performance of the adhesive bond against chemical agents, temperature changes, and internal-external mechanical deformations.

This is essentially due to the specificity of use of the bonded materials, where the stresses are endured first by the interfaces, internally at the fiber-matrix interface, at the pre-impregnated composite plies, and finally at the bonding interfaces.

The most common failure types in adhesive bonds for this industry are: interfacial failure, intra cellular buckling in the composite structures, outward face wrinkling [89].

2.8.2 Building and Construction

Many types of adhesives are in use in industry, this includes the construction industry. Some adhesives requires sophisticated application methods, while others can be applied by trowel, spray and paint coating.

Two main types of adhesives used in construction are: Structural and non-structural adhesives. Structural adhesives are required for the bonding of structural parts such as bonding of concrete to concrete, metallic structural components to concrete, and construction panels. Non-structural adhesives are used to bond decorative materials such as floors, wall covering, and materials which do not requires high strength.

Table 2.10 Most common adhesives in building industry.

Function	**Use**	**Type**
Structural timbers	Structural	Polyurethane
Ridge beams	Structural	Resorcinol-formaldehyde

Box beams	Structural	Epoxy resin
Concrete	Structural	Resin emulsions
Timber bonding	Structural	Resorcinol-formaldehyde
Steel bonding	Structural	Acrylics, epoxies
Concrete bonding	Structural	Two part epoxies
Wall covering	Non-structural	Emulsion adhesive
Roofing	Non-structural	Polyurethane foam
Drywall lamination	Non-structural	Polyurethane foam
Sealants	Non-structurural	Silicones, cyanoacrylates

2.8.2.1 Wood

Wood is a highly anisotropic material due to its pronounced fibrous structure. In the bonding process, during drying, solvents evaporates and the adhesive film conform to the wood porous structure enabling the adhesive to build up a mechanical interlocking at the interface of the two phases.

The chemical structure of the main components of wood (Cellulose, lignin) with their hydroxyl groups, offers the possibility of formation hydrogen bonds and even covalent chemical bonds in the adhesive layer [89].

2.8.2.2 Steel

Steel structural parts and laminates are a fundamental component of the construction industry. Structural parts when the bond is metal to metal most likely a

traditional welding process will be done, but when two different phases or metals that cannot be welded are bonded the use of adhesives is very advantageous.

Some of the most common interactions between adhesives and steel in construction are: adhesive anchoring systems in which a cylindrical glass capsule contains a polymer resin, a fast curing agent, and a mineral aggregate; this is inserted into a drill hole and a metallic component is inserted this can be a rebar, bolt or some structural component. Surface bonded reinforcement is a method in which steel laminates are bonded to concrete structures to give a light, fast and economically reinforce to an existing structure. Both of this methods are based in the successfully use of the adhesive and the bond strength between the substrates [90].

2.8.2.3 Concrete

Adhesives has been used in concrete adherends to join old concretes and new concretes, in injection systems which are a mixture of mortar, expanding resin, and a curing agent pumped into cracks in structural systems to rehabilitate and reinforce the structure.

Adhesives are also used to join big and heavy parts of structures like bridges. The adhesive layer between each section of the bridge contributes to reduce the stiffness of the system and facilitate the structure assembly.

Concrete composites are also used in the construction industry. Fiber-reinforced concrete is being increasingly used in the rehabilitation of concrete structural elements in the form of an externally bonded reinforcement [91].

The efficiency of the structural rehabilitation relies on the combined action of the bond between the composite element and the bond of the fiber reinforcement and the concrete [92].

2.8.2.4 Glass

Due the brittle characteristics of glass and glassy materials and the more common use of this materials in the building industry, adhesive bond offer advantages to attach glass structures to other surfaces without the use of mechanical fastening systems.

In the last three decades, structural elements in roofs, and walls made of glassy materials are being more common, this is due to the transparency of the material and architectural design.

Laminated safety glass is formed gluing together several sheets of glass with polyvinyl butyral. The panels are being bonded initially with layers of PVB films, thermally pre-laminated between heated rollers.

The use of this material that achieves a very high strength due the multilayer bond can be seeing in high rise buildings, in structural sealant glass and for bullet proof systems.

2.8.2.5 Type of Failure

Adhesives used in the construction industry can present many different types of failure, some of them are not because of the adhesive failure, they can be due surface contamination and bad application.

Table 2.11 Most common adhesives failure in construction industry.

Cause of failure	Description
Unclean surface	Most common cause of failure. The same cleaning process can contaminate the surface when the wrong surface cleaning material is used i.e. gasoline.
Tolerances too great	Gaps between adherends are too big, the amount of adhesive required to fill the gaps is too big. This can lead to mechanical deformation at the joint, finally to debond.
Surface not dry	Moisture in the surface of the adherend can reduce the adhesive bond strength.
Incorrect amount	The use of the wrong amount of adhesive can cause the failure of the adhesive bond. If the amount is too small a weak bond could be formed or an incomplete wetting of the phases, on the other hand an excess of adhesive could be detrimental to the adhesive bond strength and stability.
Assembly time took too much time	If the adhesive is applied into the two surfaces to be joined and a considerable long waiting period passes before assembly, the adhesive layer could dry out or cured before joining.
Improper positioning of adherends	When using fast curing or contact adhesives the right positioning of the adherends it is crucial due to the fast curing time.

2.8.3 Medical Industry

Adhesives in the medical sector are used in a wide range of applications where they must meet very high requirements. Medical applications can be divided into three groups according to the period of contact within the medical device, and between the

medical device and the human body: Short-term contact, medium-term contact, and long-term contact.

Medical instruments in the first category includes disposable devices, surgery instruments. They are composed of different materials that sometimes are difficult to bond such as metal alloys, medical steel titanium, and different plastics. The use of structural adhesives is sometimes the only joining technique suitable for this type of material.

Acrylic systems are often used for the manufacture of sterile disposable products and orthopedic devices. Epoxy adhesives are used for sterilizable, reusable products such as surgery instruments. The materials and adhesives must be biologically inert, resistant to corrosion and temperature [93].

Self-adhesive products such as bandages is one of the most common application of adhesives in the medical sector. PSA tapes are used to be in a medium-term contact with human body, this type of adhesives deal with challenges such as skin texture, moisture, and motion. These materials has to allow the progress of wound healing, permeable to water vapor and oxygen without lose the adhesive strength of the bond [94].

Adhesives with a long-term contact with the human body are adhesives that must have almost a permanent bond with the human body. U/V curing Methacrylate adhesives are used to as filling materials in dentistry [95].

Tissue adhesives, also remains in contact with human body for a long period of time. This adhesives must be resistant to humid environments and compatible with endogenous tissues. Methyl methacrylate adhesives has been used to bond hip joints,

while medical approved polyurethanes and neutral cure silicones are used for implantable devices [96]

Table 2.12 Most common adhesives in medical industry and their applications.

Adhesive	Type	Bond materials	Applications
-Epoxi -Acrylic -Urethane -Cyanoacrylate	Structural	- Metal, plastic rubbers - PTFE - Silicone - Skin	- Blood bag assembly - Hospital equipment - Respirators - Skin sealant
-Hot melt -Aerosol -Solvent/water based	Non-structural	- Nonwovens - Leather - Foam - Paper	- Decorative laminates - Respirators - Surgical drapes construction - Wheel chair assembly
-Non-skin use -Skin use	Pressure sensitive	- Some low surface ...energy materials - High surface energy materials - Metals - Some plastics - Skin	- Electrodes - First aid dressing - Glucose test strip - Insulin pump attachment. - Surgical drapes - Wound dressings

2.8.3.1 Type of Failure

Adhesives in the medical industry in special the ones that are in direct contact with the human body face very special requirements not just in order to be applied, but to conserve the adhesive strength and provide a stable bond.

One of the most common type of failure of medical adhesives in contact with skin is the constant moisture of skin, if this is combined with the fact that most of this type of adhesive bonds are not static, this can lead the adhesive to failure.

2.8.4 Assembly Operations

Adhesive bonding is a very useful joining method when fragile, heat sensitive materials are joined, when the materials to join have different physical and mechanical properties, when insulation is required between components, and when sealing is required simultaneously with bonding.

Adhesive joints not just offer a lightweight bond, it offer also fast application and curing time. Time reduction in the manufacturing industry is key to reduce production cost and increase productivity [97].

Assembly methods in many of the actual industries (automotive, appliances, hardware) combine adhesive bonded parts with mechanically fastened ones. Cold-setting adhesives such as two-part epoxies, metyl methacrylate, and cyanoacrylates are the most frequently used adhesives in assembly lines.

Assembly can be defined as the act of placing and fastening two or more parts together to form a useful component [98].

Adhesive bonding is an efficient, durable and economic method for assembly different types of materials. It has certain advantages over mechanical fastening in the assembly industry. This joining process does not require of any extra component, holes, and machining.

2.8.4.1 Type of Failure

Adhesive joints in assembly processes can present failure due external factors, loads, and vibrations. Multiple failure criteria can be mentioned for the failure of adhesives in this industry, but failure drastically change depending in what is being assembled and which techniques are being used for it.

Table 2.13 Most common adhesives failure in assembly industry.

Cause of failure	Description
Bad surface preparation	For some metals and plastics a surface pre-treatment is necessary. The success of the adhesive performance it is related to surface preparation. This can go from a simple operation as washing and air cleaning to complex chemical treatments on the adherend surface.
Insufficient area of bonding	The insufficient bonded area can cause the failure of an assembled component. Bond strength is not just related to the adhesive strength is also related to the contact area between surfaces.
Temperature	Changes in temperature can make the adhesive bond to fail. An adhesive with a low melting temperature will suffer of a phase transformation when high temperatures are present. On the other hand when low temperatures are present the adhesive material can become brittle and lose much of their viscoelastic properties.
Oxidative degradation	Oxidation can affect not just the interfacial contact quality between the adhesive and the adherend. If the assembly process is carried involving high temperatures can make the adhesive material susceptible to oxidation.

Imprecise positioning	If the adhesive is deposited in the wrong spot can reduce considerable the strength of the bond. In adhesive joints is desired to wet the contact area between adherends, if the adhesive wetting is partial over the contact area, the amount of stress and load that the adhesive layer have to stand is higher than when is fully covered.
Application method	The wrong selection of the application method of the adhesive has a big influence in the adhesive bond. Some assembly processes requires extreme thin layers of adhesive that can be easy deposited by spraying, a paste adhesive deposition on the substrate can result on imprecision of the assembly or in the opposite case insufficient adhesive material.
Voids in the adhesive layer	When heat cured adhesives are used, it is possible the creation of gases from solvents, volatile materials, or water vapor in the adhesive layer. Bad mixing of two part adhesives and during joining can also give place to voids in the adhesive layer.

2.8.5 Electronics

Adhesives in the electric and electronic industry can be classified into two categories: conductive, and insulating. The conductive adhesives are generally used for joining other conductive parts in the assembly process. This conductivity does not just refers to electrical conductivity, some electronic devices use adhesives layers in the microchips that are thermally conductive to dissipate heat.

Insulating adhesives, are used for the protection of exposed circuits, wires and electronic parts. Insulating adhesives must have high electrical-thermal resistance and a very high flexibility.

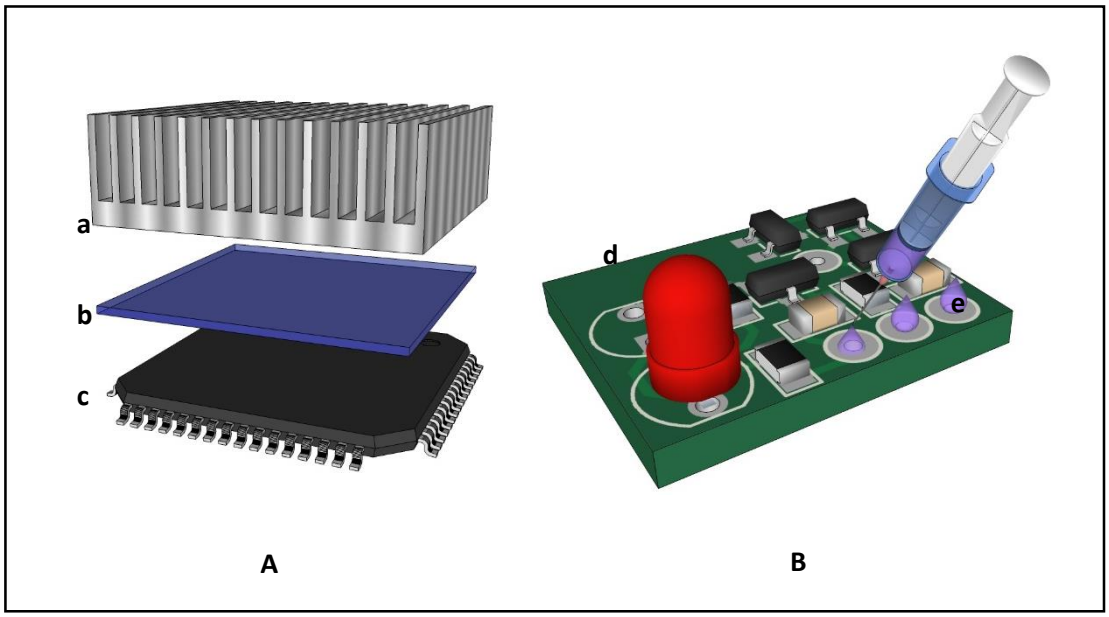


Figure 2.38 Thermally and electric conductive adhesives. (A) Thermally conductive adhesive in a microprocessor chip, (a) Heat dissipater, (b) Thermally conductive adhesive, (c) Microprocessor. (B) Electrically conductive adhesive used in a PCB board. (d) PCB board, (e) Electrically conductive adhesive.

Non-conductive adhesives can be represented by almost all the laminate PSAs and some epoxies. Electrical tape, is the best example of a laminated non-conductive PSA. Two parts epoxy used for structural application of electrical and non-electrical parts is also a good example of non-conductive adhesives.

To guarantee the non-electrical conductivity of the adhesive does not present a big challenge to the adhesive industry, the challenge starts when good conductive properties are required.

To face the conductivity requirement a variety of adhesive materials with nickel, carbon powders, and some metal particles has helped to overcome this difficulty. Shape

of the conductive particle has a big influence in the conductivity properties i.e. silver is generally used in very small flakes form to minimize cost and give higher number of contact points to improve conductivity, also the flake shapes tends to orient parallel to the adherend surface during bonding [99].

Different types of conductive adhesive materials are available for this industry from liquid glues, pastes to conductive PSAs.

Table 2.14 Most common conductive adhesives.

Type	Description
Thermally conductive adhesive	This adhesive is used in high performance electronic devices, microprocessors and in circuits with a high density of components. High heat concentrations are generated in this devices. The adhesive must be able to transfer the heat from the electronic component to the dissipation device.
Underfill materials	Electronic components with solder bumps, must remain stable during service life. The gaps between the PCB and the electronic component is filled with this type of epoxy adhesive with high thermal conductivity, shock and vibration resistance.
Electrically conductive adhesive	Electrically conductive adhesives provides stronger and tougher bonds than most soldering materials. Aluminum powder, silver-filled adhesives are used to provide good conductivity.

PSA tapes	This type of adhesive offers a versatile option to interconnect circuits in an electronic system. Adhesive films can contain conductive fibers, metalized particles and circuit diagrams. They can be isotropic when all directions are conductive or anisotropic when conductivity is just thru the thickness of the material.
Circuit adhesive labels	Circuit boards requires of labels to identify parts, use, manufacturing origin among others. Circuit adhesive labels are used for this. They have to preserve a stable bond during thermotransfer and soldering process with temperartures up to 260°C.

2.8.5.1 Type of Failure

Adhesives in the electronic industry can present different failure modes. In conductive adhesives the main two failure modes are when the adhesive do not conduct and when conduct in the wrong direction [100].

Other types of failure that are presented in adhesives in the electronic industry such as: delamination, poor adhesion and mechanical stresses can be causes of the delamination of the adhesive. This may be occasioned by incorrect selection of the adhesive material, contaminants in the substrate, moisture or low melting point in the adhesive.

Polymer degradation due to possible moisture diffusion into the adhesive material can cause the decrease of the glass transition of the polymer, this can lead to thermally induce damage and reduction of the adhesive strength [101].

The addition of a metallic phase into the adhesive can bring oxidation within the adhesive structure. This can lead to incomplete interconnection and compromise the

conductivity, also oxidation close to the adhesive interface can compromise the strength of the bond [101].

Voids and air bubbles, can be originated by too high rate and speed of heating this can reduce considerable the conductivity of the material and introduce vacancies in which the adhesive bond can start to fail [102].

2.8.6 Consumer DIY

Consumer end or do it yourself (DIY) adhesives are also called household adhesives. These are used for gluing, assembling, and repairing a variety of materials in the household.

DIY adhesives include a very wide selection of adhesives materials, and presentation. They could be packed as tubes, tapes, liquid glues, and pastes.

Table 2.15 Most common consumer DIY adhesives.

Type	**Description**
Craft glue (liquid, solid)	Cellulose derivatives, polyurethanes.
Multipurpose adhesives	Polyurethane and acrylate dispersions.
Tapes and pads	Pressure sensitive adhesives.
Super glues	Cyanoacrylates
Hot melts	Ethylene-vinyl acetate with tackyfiers, silicones
Two component adhesives	Two part epoxy.
Contact cements	Polystyrene-butadiene with phenolic resins, polyurethanes.
Plastic adhesives	Butyl acetate
Wood glues	Poly vinyl acetate

2.8.6.1 Types of Adhesive and Failure

In the consumer DIY there are many different adhesive materials depending of the final usage, depending on it the mechanism of failure will behave distinctly.

2.8.6.1.1 Craft Glue

Craft glue is used for gluing paper materials like card board, pictures and paper sheets. It can be found dispensed as a liquid glue or as a semi-white glue sticks. Most of this adhesives are solvent-free, contains a soap gel as builder, and natural or synthetic polymer as adhesive material.

Craft glue adhesive failure can be related to excessive application, long drying time, bad temperature resistance, and high sensitiveness to liquids and moisture.

2.8.6.1.2 Multipurpose Adhesive

Multipurpose adhesives are used to bond most materials from cardboard to textiles, metals and plastics; usually used in small scale assembly and handicrafts. The strength of the bond is related to the materials that are being bonded.

This adhesives can fail due to interfacial incompatibility with the substrates, moisture, and temperature changes.

2.8.6.1.3 Tapes and Pads

Tapes and pads are PSA type of adhesive. In the consumer DIY industry this materials are supplied in many different presentations and sizes, with single coat, double coating and reinforcement.

They consist as a normal PSA of a carrier, an adhesive coating, and in some cases a reinforcement. The failure of this type of adhesive can be attributed to weak bonding during lamination, contaminants in the interface between adherend and adherent, stiffness of the backing material, environmental factors and variations in temperature.

2.8.6.1.4 Super glues

This type of adhesive is used for repairing work, they are suitable for small repairs and very unlikely will work to fill gaps or thick bonds. The drying time is very fast and once dried out provides a very strong bond, without influence of surface roughness of the substrates, they can be presented in liquid or gel form.

Super glues main ingredients are cyanoacrylates, when they dry, they become a very brittle bond. Failure can occur when flexibility is required and due to the rapid drying time if the substrates are not bonded together fast enough it can result in an incomplete or weak bond.

2.8.6.1.5 Hot Melts

Hot melts are the types of adhesives in the DIY market that generally are applied with the use of a high temperature gluing pistol, when the adhesive is melted and applied after a short period of time a good adhesive strength can be obtained.

The use of high temperature to apply this type of adhesive can lead to the melting or damage of the substrate causing the failure of the interfacial bond or fusion of the surfaces.

If the adhesive is applied not at the right temperature the material will not have the adequate viscosity to conform to the surface also leading to failure of the adhesive.

2.8.6.1.6 Two Component Adhesives

Two component adhesives are used when a very strong and durable bond is needed. A common use of this adhesives is repairing and gap filling in materials considered strong such as metals, and a strong bond is needed.

Usually a two part epoxy after curing exhibit a strong but brittle bond. Failure in this type of adhesive can be due to improper mixing of the components or by interfacial failure between the adhesive and the substrate

2.8.6.1.7 Contact Cements

Contact cements are generally used when larger and heterogeneous materials have to be bonded, when joining difficult parts, and when laminating covers or materials to the surface of the adherend.

This types of adhesives are dispensed in different viscosities, it requires of solvent evaporation to provide a good bond, if the adhesive is applied in excess or let it dry for too long the strength of the bond is compromised and failure of the adhesive can occur.

2.8.6.1.8 Plastic Adhesives

This type of adhesive is used to bond almost all plastics. Their adhesion mechanism is based on the use of solvents to slightly dissolve the surface of the materials to be bonded, it can be called a solvent-welding adhesive.

Failure of the adhesive bond can occur by insufficient amount of adhesive material or by the not reaction of one of the substrates with the solvent. If an excessive amount of adhesive material is used damages to the surface of the material can be made.

2.8.6.1.9 Wood Glues

This type of adhesive is generally a water based adhesive, it is used to repair and join wooden materials. After adhesive application the parts must be cold or hot pressed for certain amount of time.

2.8.7 Packaging

Packaging materials and graphic products are essential for handling, distributing and storage manufactured goods. In the packaging industry adhesives must have a good performance in a wide range of materials or substrates.

The adhesive material must withstand conditions to which the final packed product will be exposed such as: high loads and stresses, mechanical deformation, environmental changes such as humidity and temperature, all of this preserving a good relationship between performance and price.

Adhesives are not just in the final packaging of the goods in form of tapes, it is also used in the manufacturing of the cardboard. The one is a multi-laminar composite which is composed of two flat laminas and a one or more corrugated cores.

There are two broad types of adhesives used in the packing industry the ones that are used to make the packaging material, and the ones used to seal the packages.

Table 2.16 Most common adhesive applications in the packaging industry.

Application	Description
Manufacture of corrugated board	Starch based adhesives used during the corrugating and lamination process. When special strength and performance requirements in packaging are needed, emulsion based or hot melt adhesives are used.
Coating of cardboard and paper	Polyacrylate emulsions and hot melt adhesives are being used for this application because they are solvent free. This is used for heat or moisture sealable applications.
Paper sacks assembly	For this application starch based adhesives are used for the longitudinal section of the sack, while for the bottom starch or some water based emulsion can be used.
Envelopes	The adhesive used in the back of the envelopes is a mixture of dextrin glues and mixed emulsions, which dry more quickly. Moisture activated hot melts are also used for this application.
Automatic packing machines	Emulsion based and hot melt adhesives are used for this application. Hot melts are the preferable choice due their fast setting
Laminating films	This type of adhesives are produced by lamination or extrusion. In the first one the low viscous adhesive material is applied to the laminate by rolls. In extrusion a polymer melt is extruded onto a primary web. Moisture activated polyurethanes are often used for this application.
Labeling of plastic containers	Adhesives used for this application must have good adhesion to low surface energy materials. Polyethylene, polypropylene and polyethylene terephthalate are the most common adherends.

2.8.7.1 Type of Failure

Moisture in adhesives in the packaging industry can be one of the main failure causes. In labeling, this can generate a weak bonding with the adherend due to the moisture activation nature of the adhesive material.

In cardboard manufacture and envelopes moisture also can generate debonding between the laminates. Surface contaminants like dust and other particles can deteriorate the bond quality and compromise the adhesive performance.

2.8.8 Tape and Label

Tape and label is one of the biggest industry in the use of adhesives there are different types from industrial tapes to labels in products and packing material.

2.8.8.1 Labels

Industrial tapes were introduced into market in the 1920s and 1930s, self-adhesive labels in 1935 [96]. This type of adhesives are categorized as pressure sensitive adhesives, the number of applications in which PSAs are almost uncountable.

The product form and the stiffness of the backing influence completely the application and adhesive performance of tapes and labels. The application of pressure sensitive labels generally is cold laminating process, it involves the use of adhesive-backed carrier on a release liner.

In the label industry exist a difference between roll and sheets laminates. Adhesive requirements for roll applications are generally less critical then sheet applications in

which it is required a strong bond to prevent self-delamination, but present a moderate tackiness.

The most common adhesives in this industry could be: single side adhesive, double side adhesives, adhesive pads, medical tapes, and labelstock.

Table 2.17 Most common types of pressure sensitive labels

Label type	**Description**
Temperature resistant	Used for surfaces that are exposed to high temperatures, generally between 40 °C and 260 °C.
Freezer labels	This labels have a special composition that ensures the adhesive flow and bonding at low temperature. This type of labels has to preserve their viscoelastic properties in temperatures between -40°C to 20°C.
Water resistant	This type of labels are used in application which will expose it to water and moisture such as: bottle labels, cars, and to mark textiles.
Price and weight	This is one of the most popular and dynamic application for labels. There is a big variety of requirements for this application. The adhesive in the label have to be able to perform in big variety of surfaces and roughness.
Nameplates	This type of label is used to identify brands, type of device, production lot, or specific information regarding equipments, apparatus or electrical appliances. It is necessary to be chemically-water resistant with a writable surface and withstand abrasion.

Informational labels	This type of label is used in many fields, it is used to print information or instructions about a specific object or subject for the final costumer. This can be medical, assembly or usage instructions.

2.8.8.2 Tapes

Tapes are PSAs with a structural facestok that provides the reinforcement of the adhesive system, used to provide structural integrity, dimensional stability, and shape retention. In tapes the mechanical strength of the facestock is as important as the adhesive strength of the coating on it. Tapes are a composite material that can have from one to many layers of similar or dissimilar materials, the ones are also bonded between them.

The amount, type and construction of the reinforcement layers is on depend of the final application of the system. This PSAs does not require any type of curing or post processing, once applied the adhesive bond is stablished between the surface of the adherend and the adhesive layer of the tape [103].

The application process of tapes and labels involves the process of delamination and lamination. The pressure sensitive adhesive is delaminated of the carrier or the protecting laminate, then being laminated into the surface of the adherend material.

As discussed before for labels the quality or type of facestock material is not incidental to the application process. Labels are applied by delaminating a multi-web composite: the adhesive layer coated into the carrier, and the release coated surface. On the other hand for tapes the delamination process consist of unwinding.

The quality and mechanical properties of the non-adhesive backing material is determinative for the delamination-lamination process and for the performance of the adhesive system [103], the winding up process of tapes dictates the required amount of pressure necessary to adhere by lamination into the substrate [104].

Table 2.18 Most common types of pressure sensitive tapes.

Label type	**Description**
Packaging tapes	This is a tape with a carrier that has good mechanical strength, non-deformability coated with a high molecular weight polymer coating.
Tear tapes	Self-adhesive tear tapes are designed to be used as an easy opening interface for flexible packaging. They can be used to remove the top of a package or to form a lid.
Repair tapes	These are flexible tapes with a laminar or fiber reinforcement. They are designed to withstand high strength applications and tear, with a good conformability providing good bonding to substrates such as: metals, wood, ceramics and plastics.
Insulating tapes	This type of tape is used to insulate heat or electrical wires or as sealants. They have to present good mechanical strength, flexibility, thermal and chemical resistant.
Mounting Tapes	This type of tape is used to mount parts during an assembly process. They can be single or double sided, and must present high temperature, good environmental resistance, and high conformability.

Medical tapes	This kind of tapes are flexible tapes with special properties such as: breathable, good cohesive strength, good conformability, and they cannot be degraded by the interaction with body fluids.
Repositionable tapes	This type of tapes can have many different kind of applications, they can also work as a mounting tape. The most representative requirement is the ability of laminate and delaminate from one substrate to other with different surface roughness and properties.

2.8.8.3 Type of Failure

This type of adhesives present different failure mechanisms some of them are related to the type (static, dynamic) and direction (shear, peel) of the load, temperature and environmental factors.

There are some failure mechanisms that they are unique characteristics of certain type of tapes or label. This will be driven by the material used to conform the adhesive system, the adhesive material and the manufacturing process of the adhesive.

Table 2.19 Common adhesive failures of tapes and labels.

Type of failure	**Description**
Interfacial debonding	This type of failure not just occurs when the tape or label experience shear loads. This also happens when the adhesive layer debonds from the facestock due to incompatibility of the phases, or by melting of the adhesive layer. This is more common in laminar PSAs.

Debonding from the adherent	This type of failure occurs when the lamination process is not performed correctly or when solid or liquid contaminants are present in the surface of the adherend. This can cause that the adhesive bond is made between the PSA and the contaminants, not with the adherent surface.
Failure of the facestock	This occurs when the backing of the PSA experience deformations that compromise the structural performance of the adhesive system. If the tensile strength of the backing is too low, most likely the PSA will present ruptures, deformations or elongations that will destabilize the adhesive system compromising the adhesive bond and strenght
Failure by stiffness	The stiffness of the facestock has an important role in the conformability of the adhesive layer to the substrate surface. If the backing is too stiff the adhesive cannot conform well, depending of the type of adhesive layer, the adhesive can auto-delaminate after application.

2.9 Existing Repositionable Adhesives in Consumer Industry

The demand for adhesives materials that can delaminate from a substrate multiple times conserving their adhesive strength without damaging the substrate surface has become of extreme interest for industry and researchers.

Repositionable adhesives are designed to form a temporary bond, the one can be delaminated after a certain period of time without leaving residue on the adherend. This type of materials are generally designed to have low adhesion strength, therefore cannot hold much weight.

Many different approaches has been utilized to produce this kind of materials in a cost effective way the most representative are: pressure sensitive adhesives laminated in a film, single and multi-laminar composites with a non-deformable foamy laminates coated with liquid acrylic adhesive, multi-laminar composite with a rubbery adhesive interface, hooks and loops, and pressure sensitive adhesives coated on deformable foamy laminar structure.

2.9.1 Pressure Sensitive Adhesives Laminated in a Film

Repositionable pressure sensitive adhesives are PSAs laminated in a flexible facestock. The flexibility of the facestock and the tackiness of the adhesive layer permits the removal of the whole adhesive system generally without damaging the surface of the substrate.

Due their tacky adhesive, during delamination from the substrate residual adhesive can be left on the substrate surface, a schematic representation of PSAs coated in thin films can be found in figure 2.1.

The cohesive failure of the material compromise the adhesive system performance, reducing the strength of the bond and the reusability of the material, besides the possible damage to the surface of the adherend.

2.9.2 Single and Multi-laminar Composites with a Foamy Laminate

This type of removable adhesive is based in a laminar composite in which the external faces of the composite are coated with a thin low glass transition temperature adhesive layer.

The laminar foamy composite is usually used for applications that requires low loading demands in which either the adhesive strength or the structural integrity of the adhesive system is not fully compromised.

The multi-laminar foamy composite follows the same structure of the single lamina, but with the incorporation of one or more reinforcement layers.

This reinforcement layers could be formed by fibers, plastic, or metallic thin films, this with the goal of enhancing the adhesive system performance and structural strength for higher loading demands.

During the lamination process this adhesive material works as a double sided pressure sensitive tape, but during delamination the foamy laminate can be stretched, this will compromise the structural integrity of the material, making difficult the reapplication of it.

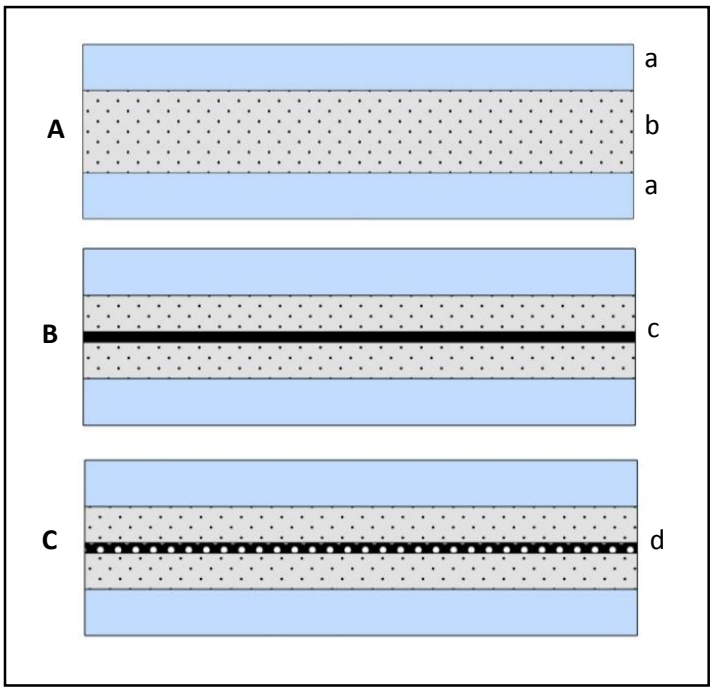


Figure 2.39 Schematic representation of single and multi-laminar foamy composite repositionable adhesives. (A) Single foamy layer, (B) Multi-laminar composite with a thin film as reinforcement (C) Multi-laminar composite with a fibers as reinforcement, (a) Adhesive layer, (b) Foamy layer, (c) Film reinforcement, (d) Fiber reinforcement.

2.9.3 Multi-laminar Composite with a Rubbery Adhesive Interface

This repositionable adhesive is also based on a laminar composite structure, it can be divided in two very well defined components: the structural system and the adhesive system.

The structural system is constituted by a set of rigid plastic laminates from different thickness, this also works as a composite laminar facestock, providing the reinforcement for the system.

The adhesive system is composed by a highly viscoelastic rubbery layer, sometimes this layer can have macro or micro patterns.

Figure 2.40 Schematic representation of multi-laminar composite with a rubbery adhesive interface. (A) Laminar component, (B) Laminar component, (C) Rubbery adhesive interface.

2.9.4 Pressure Sensitive Adhesives Coated on Deformable Foamy Laminar Structure

This type of repositionable adhesive is composed by a single layer foamy material coated on both sides with a pressure sensitive adhesive. The foamy phase will contribute to the flexibility of the adhesive system during conformation to the surface of the adherend, providing at the same time a reinforcement layer the one is also used as a release mechanism, when plastic deformation is induced.

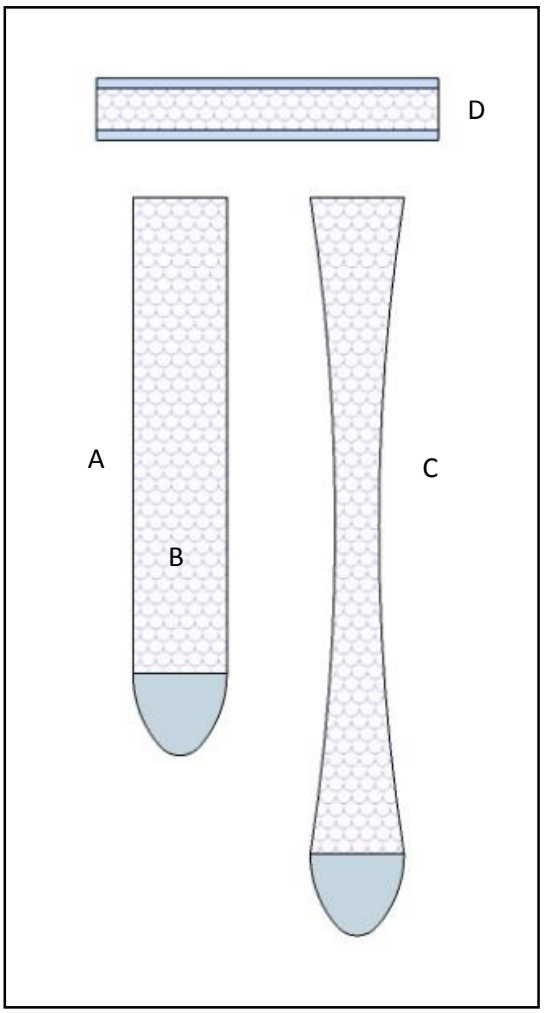


Figure 2.41 Schematic representation of pressure sensitive adhesives coated on deformable foamy laminar structure. (A) Non-deformed repositionable adhesive, (B) Foamy phase, (C) Plastically deformed foamy phase, (D) Cross-sectional view of the foamy component coated with the adhesive layer.

CHAPTER III

EXPERIMENTAL WORK

3.1 Materials

Termoplastic polyurethane (Desmocoll 500/2) provided by Bayer Materials Science, tetrahydrofuran (THF) C_4H_5O purchased from VWR international, IKA C-MAG HS 7 magnetic stirring plate with controlled temperature from VWR, and Acrylic PSA from Chemsultants were used to prepare the polymer solution.

5ml plastic syringes from Cole-Parmer, JG20-2.0X needles from Jensen Global, a high voltage power supply from Gamma High Voltage research technologies, variable voltage CSI3005T DC power supply from circuit specialists, syringe pump acquired from Fisher Scientifics, rotating grounded collector, and aluminum foil used as facestock was used for the electrospinning process.

JEOL JSM 6510LV scanning electron microscope, and AMSCOPE 1400 optical microscope was used to characterize and observe the microstructure of the electrospun nanofibers and repositionable adhesive samples, KYOWA DropMaster DMs-200 contact angle was used to measure the contact angles.

A dynamic shear tester DS1000 from cheminstruments was used to measure the shear adhesion of the samples and the built peeling testing device were used to perform the peeling strength measurement and to delaminate the samples from the substrate.

3.2 Electrospinning Process

The polymer solution was prepared using a mix of thermoplastic polyurethane (10 wt%) with the acrylic PSA (5wt%) dissolved into THF, the solution was stirred 24 hours in a magnetic stirring plate at room temperature.

The solution was loaded into the 5 ml plastic syringe with an internal diameter of 12.30 mm, a JG20-2.0X needle with an internal diameter of 0.635 mm and length of 25.4 mm.

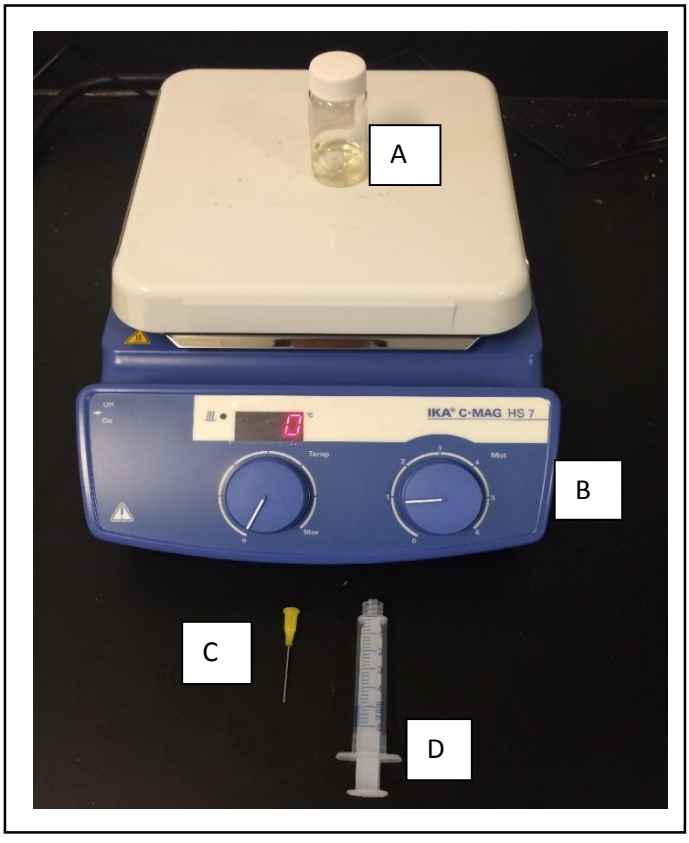


Figure 3.1 Solution preparation. (A) Solution vial, (B) IKA C-MAG HS 7 magnetic stirring plate with controlled temperature, (C) JG20-2.0X needle, (D) 5 ml syringe.

For the electrospinning process, a grounded rotating collector was used, the distance between the tip of the needle and the surface of the collector was 175 mm.

The needle was positive charged using the high voltage power supply to a fixed voltage of 17 kV, samples were taken with a linear speed of 9 m/s. The electrospinning time was of 45 minutes, solution is pumped by a syringe pump with a controlled flow rate of 0.40 ml/h.

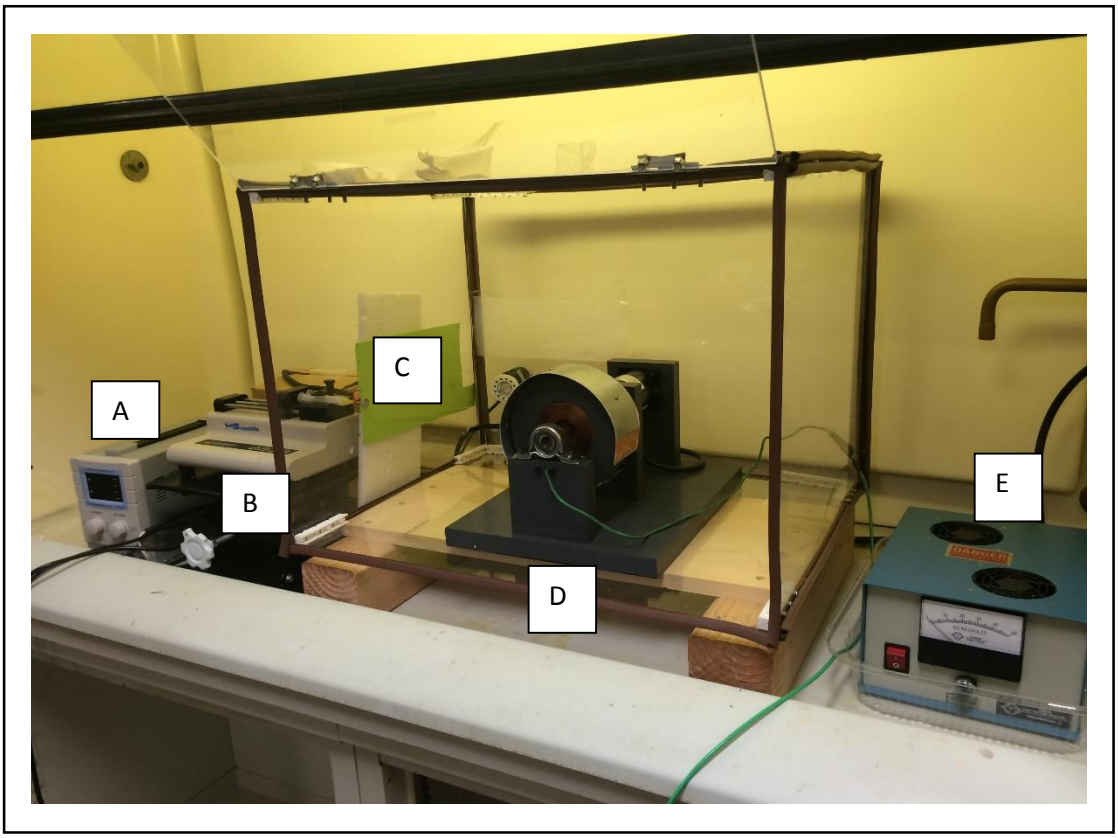


Figure 3.2 Electrospinnning setup. (A) Variable voltage CSI3005T power supply, (B) Syringe pump, (C) JG20-2.0X needle, (D) Rotating collector, (E) Gamma high voltage power supply.

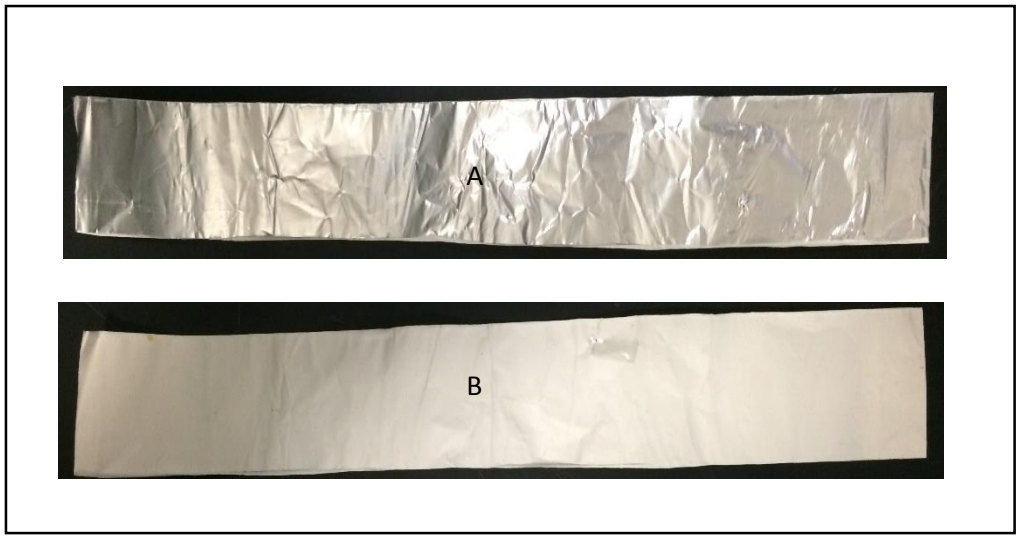


Figure 3.3 Electrospun nanofibers sample. (A) Non-coated aluminum foil, (B) Electrospun nanofibers coated on aluminum foil.

3.3 Scanning Electron Microscope

For the characterization of the morphology of the electrospun nanofibers a JEOL JSM 6510LV scanning electron microscope was used, samples were sputtered with an Emitech sputter coater. The voltage used for the imaging capture was 15 kV, with a magnification of 1000X.

Figure 3.4 JEOL JSM 6510LV scanning electron microscope.

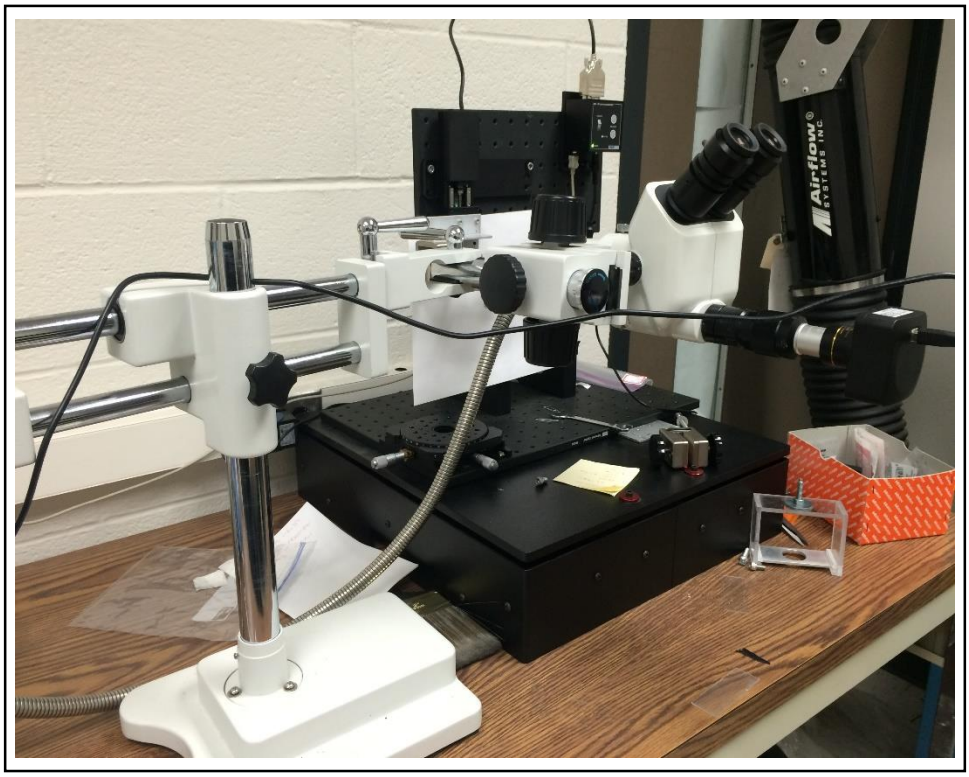


Figure 3.5 AMSCOPE 1400 optical microscope.

3.4 Contact Angle Measurement

The contact angle of the electrospun samples, substrate and repositionable adhesives was measured using a KYOWA DropMaster DMs-200.

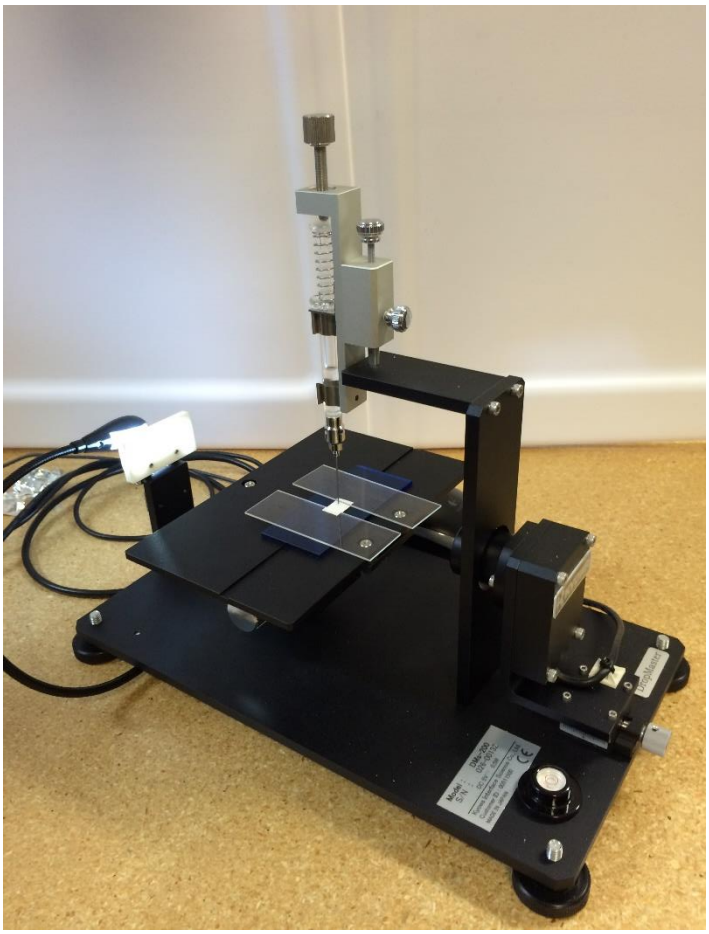


Figure 3.6 KYOWA DropMaster DMs-200 contact angle measurer.

3.5 Adhesion Testing

The adhesion testing was carried out with the use of a dynamic shear tester from cheminstruments, and a peeling device assembly able to peel in 90° and 180° degrees.

3.5.1 Dynamic Shear

The DS1000 dynamic shear tester was used to measure the shear adhesion, samples were cut to 10 x 15 mm, and positioned on the steel plate substrate. The instrument was calibrated using two known calibrated weights before testing.

Figure 3.7 DS1000 dynamic shear tester.

3.5.2 Peeling Test

For the peeling test, an in house device was built capable to perform 180° and 90° peeling. The device is composed of two main parts: the base part were the substrate is positioned and the upper part, the one that is the adjustable fixture depending of the peeling

angle, this device were used to delaminate the samples using a controlled peeling force, under the Amscope UM1400 microscope.

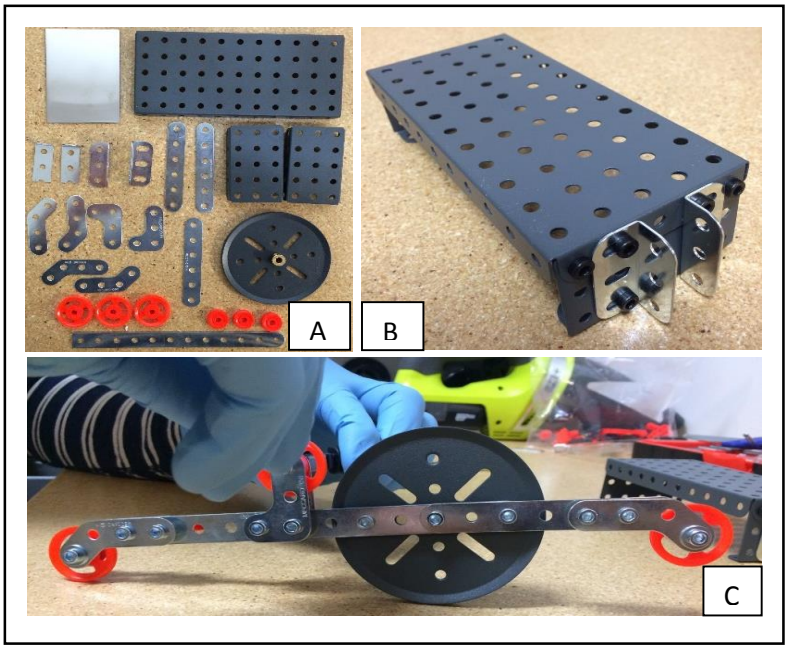


Figure 3.8 Peeling device parts and assembly. (A) Component parts, (B) Base part, (C) Upper part.

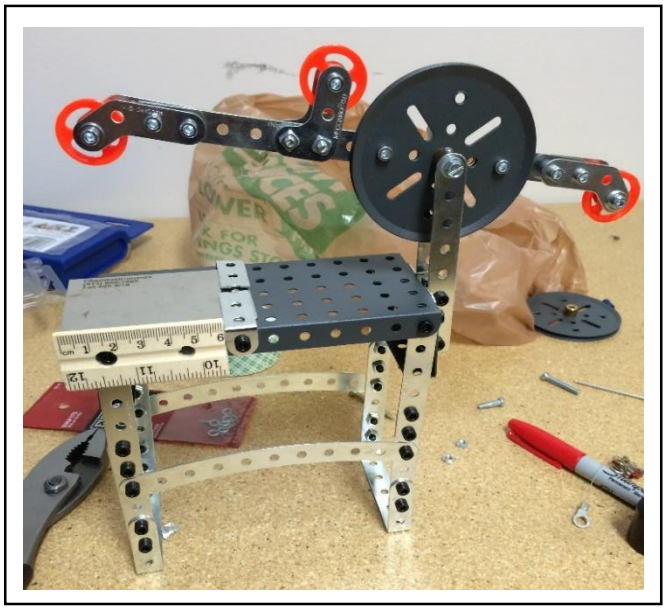


Figure 3.9 Assembled peeling device.

CHAPTER IV

RESULTS AND DISCUSSION

Four different types of samples were analyzed on how they laminate and delaminate from the substrate for being compared with the electrospun fibers sample:

Table 4.1 Classification of samples.

Sample 1	Adhesive composite with a foamy laminate
Sample 2	Electrospun nanofibers
Sample 3	Multi-laminar composite with a rubbery adhesive interface
Sample 4	Pressure sensitive adhesive coated on a deformable foamy laminar structure
Sample 5	Pressure sensitive adhesive laminated in a thin film

4.1 Adhesion Testing

Two different adhesion measurements were performed to the samples: dynamic shear adhesion and peel strength at 90 and 180 degrees.

4.1.1 Dynamic Shear Test

From the dynamic shear test it was possible to find that the samples 1, 4 and 5 have similar shear strength values, being sample 2 the highest and sample 3 the lowest, this results are discussed later in this section.

The average values are:

Table 4.2 Average Dynamic Shear Strength.

Label	Description	N/cm^2
Sample 1	Foamy laminate	15.67
Sample 2	Electrospun fibers	29.44
Sample 3	Multi-laminar composite with rubbery interface	1.05
Sample 4	Deformable foamy laminate	16.34
Sample 5	Thin film	8.36

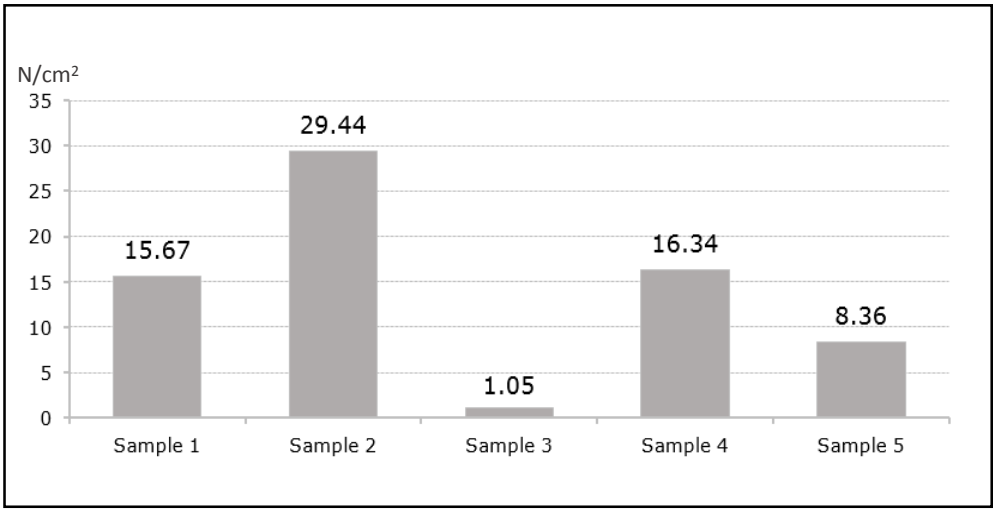


Figure 4.1 Dynamic shear strength.

4.1.2 Peeling test

The samples were positioned on the built peeling device to measure the peeling strength at 90 and 180 degrees, using calibrated weights.

The average values for the 90 degrees peeling are:

Table 4.3 Average 90° peeling strength.

Label	Description	N/cm^2
Sample 1	Foamy laminate	13.10
Sample 2	Electrospun fibers	0.06
Sample 3	Multi-laminar composite with rubbery interface	0.21
Sample 4	Deformable foamy laminate	17.36
Sample 5	Thin film	0.50

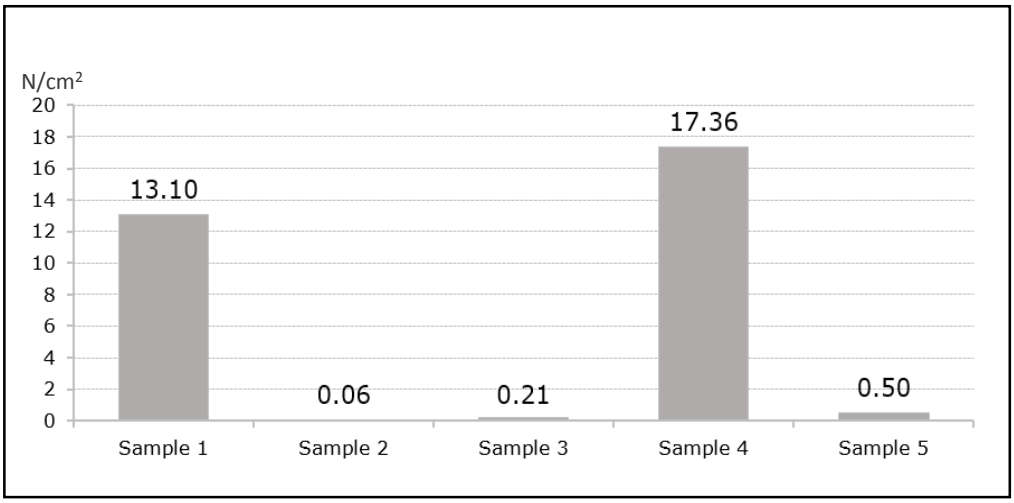


Figure 4.2 Peeling test average values (90 degrees).

Table 4.4 Average 180° peeling strength.

Label	Description	N/cm^2
Sample 1	Foamy laminate	9.86
Sample 2	Electrospun fibers	0.01
Sample 3	Multi-laminar composite with rubbery interface	N/A
Sample 4	Deformable foamy laminate	5.94
Sample 5	Thin film	0.11

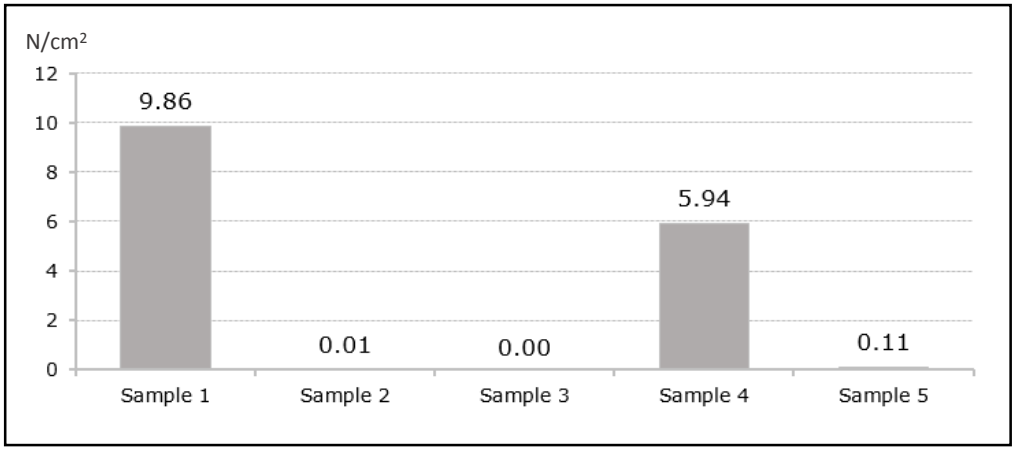


Figure 4.3 180 degrees peeling test average values.

From the summary of the performed adhesion test it can be seeing that the electrospun nanofibers has a different behavior in comparison with the other adhesives in the relationship between shear and peel strength.

The electrospun nanofibers exhibit a considerable high shear strength and a extremely low peel strength.

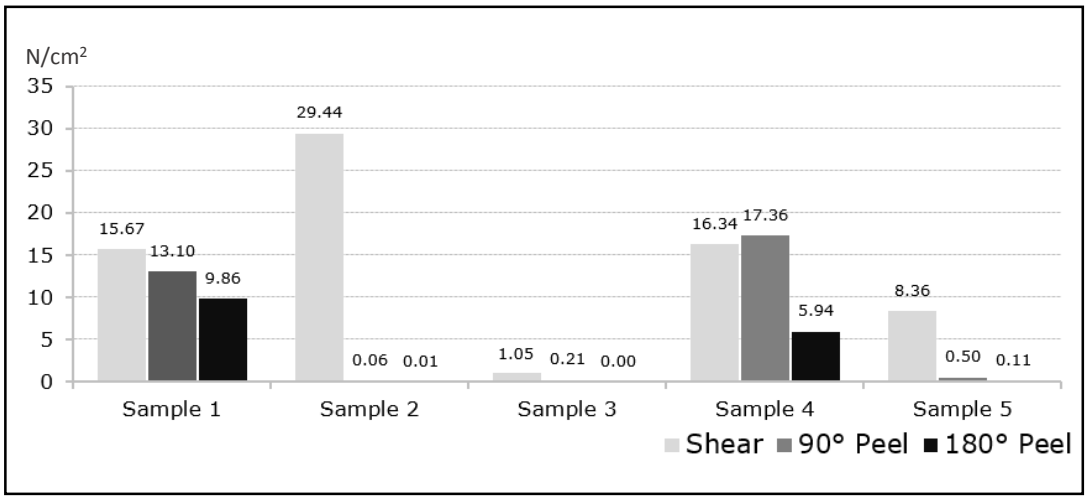


Figure 4.4 Summary of adhesion test.

4.2 SEM Analysis

To understand the difference in the results of the adhesion tests performed, the morphology of the surface of each sample is investigated thru scanning electron microscope, and during the process of lamination and delamination thru optical microscope.

Scanning electron micrograph of the foamy laminate is presented in figure 4.5. It is possible to identify that the adhesive layer of the composite is a continuous phase, laminated in the foamy phase. This makes the composite behave as a whole system, it is also found that the foamy phase is a phase free of perceptible voids.

In the surface of the adhesive layer it was found a high density of cavities, this can contribute to the adhesive strength creating a micro-suction effect.

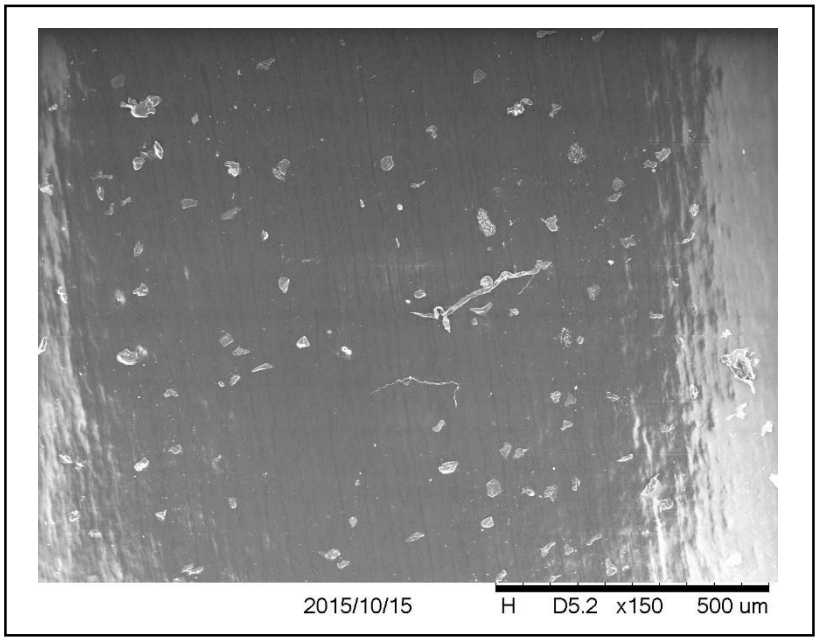


Figure 4.5 Foamy laminate adhesive scanning electron micrograph.

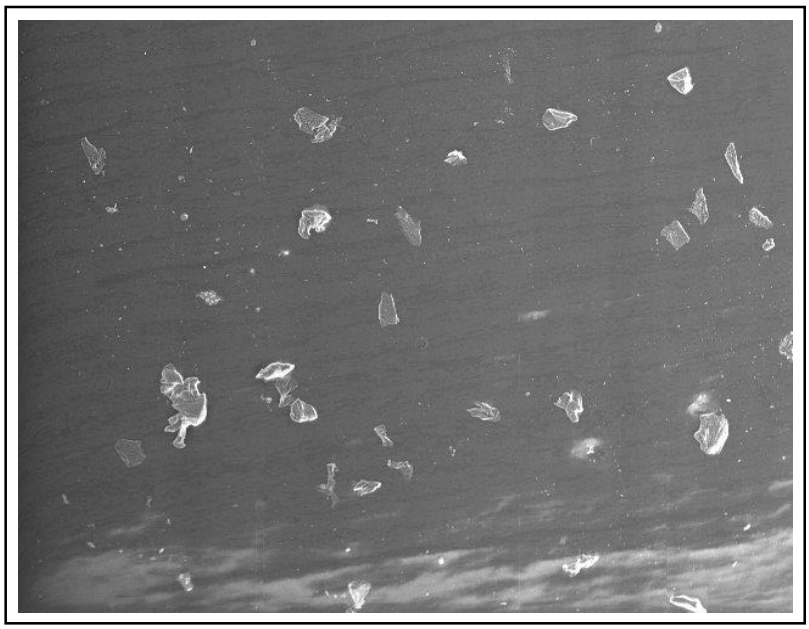


Figure 4.6 Higher magnification SEM micrograph of surface cavities.

Figures 4.7, and 4.8 illustrate the surface morphology of the electrospun nanofibers. It is possible to visualize that from collecting the fibers with the rotating drum has drawn and given certain degree of alignment to the nanofibers.

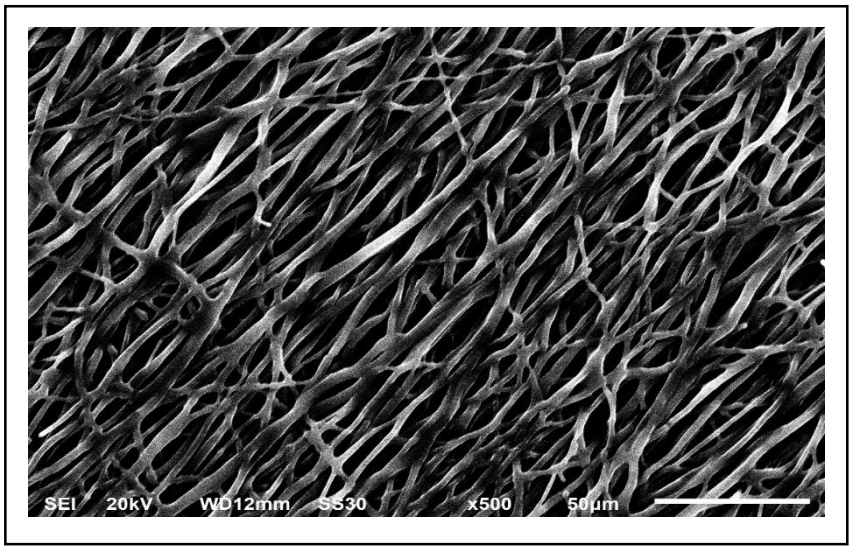


Figure 4.7 Electrospun naofibers ESM micrograph 500x.

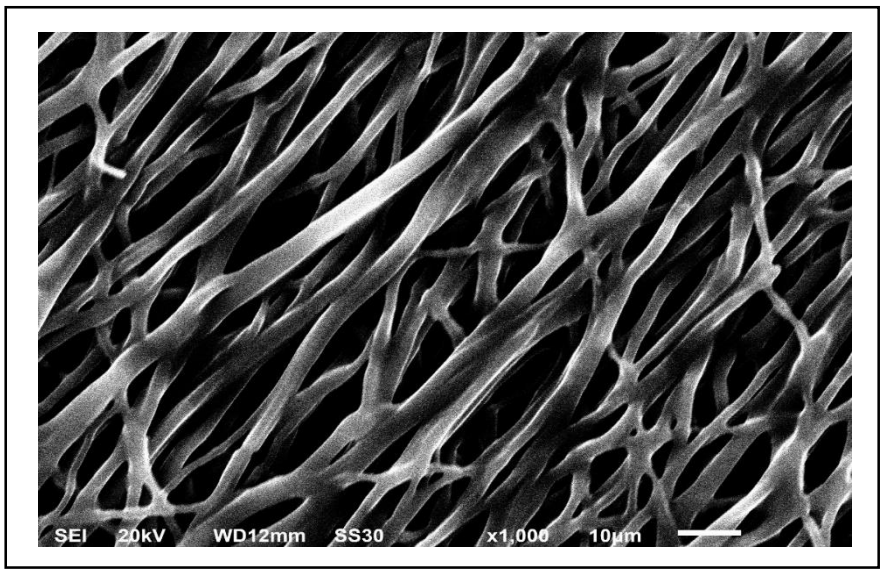


Figure 4.8 Electrospun naofibers ESM micrograph 1000x.

The morphology of the multi-laminar composite with a rubbery adhesive interface was analyzed under the SEM, and it is shown in figure 4.9.

It is possible to see that rubbery interface doesn't have any texture or nano-micro pattern and it's a continuous phase. Due to lack of visual reference, a second SEM micrograph in which a reference point its seeing was taken, also to discard sample melting.

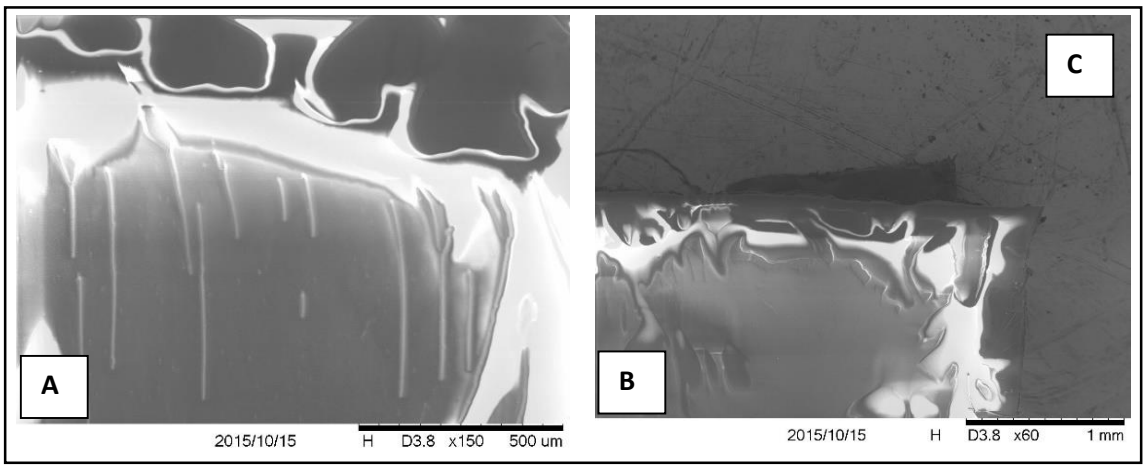


Figure 4.9 Multi-laminar composite with a rubbery adhesive interface ESM micrograph. (A) Adhesive interface 150x, (B) Adhesive interface 60x, (C) Sample holder.

Scanning electron micrographs of the deformable foamy laminate adhesive sample are shown in figures 4.10. It was found that in the foamy laminate, the one which provides the structural stability of the adhesive system has a pattern of aligned micro voids all over the surface.

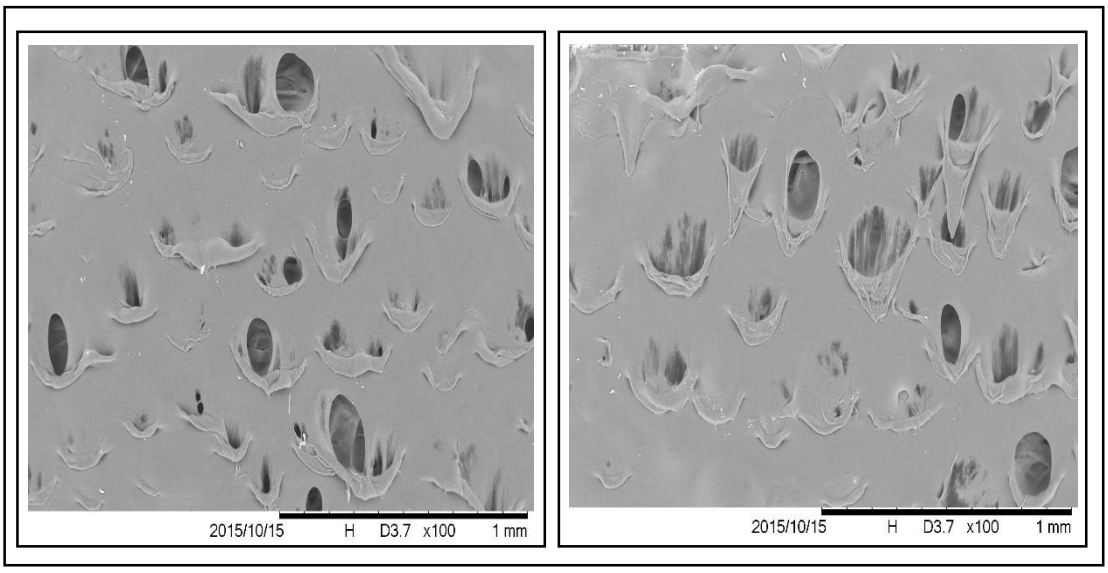


Figure 4.10 Surface morphology of deformable foamy laminate adhesive.

These micro voids allows the reinforcement to be plastically deformed causing the delamination of the sample from the substrate surface, in figure 4.11 white lines indicates the alignment of the micro voids in the sample.

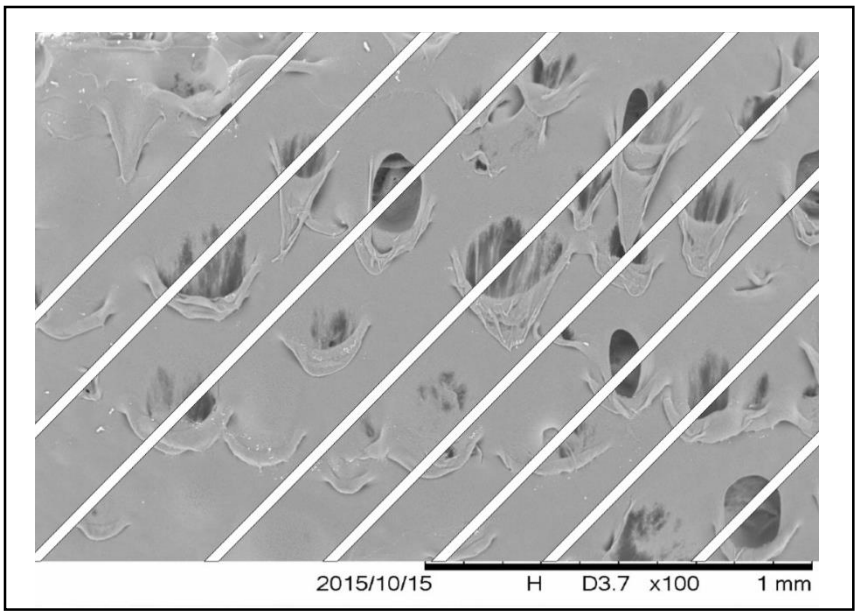


Figure 4.11 Micro voids alignment

4.3 Contact Angle

Contact angle measurements were taken from the electrospun nanofibers and the repositionable adhesives to analyze the wetting properties of the adhesive surface.

It was found that the non-deformable foamy laminate repositionable adhesive present a contact angle of 106.6° when measured. This can be characterized as a hydrophobic surface. Electrospun fibers presented a contact angle of 128.1° being characterized as a super hydrophobic surface.

Multi-laminar composite with rubbery interface presented a contact angle of 101.3, Deformable foamy laminate presented a contact angle of 100.6, being this two characterized as hydrophobic surface.

The surface of these four samples can be categorized as a low surface energy, this based on the concept that contact angle is inversely related to surface energy.

For the coated thin film sample, it was measured a contact angle of 57.3°, being this the only sample with a high surface energy.

Table 4.5 Contact angle values.

Label	Description	Θ°
Sample 1	Foamy laminate	106.6
Sample 2	Electrospun fibers	128.1
Sample 3	Multi-laminar composite with rubbery interface	101.3
Sample 4	Deformable foamy laminate	100.6
Sample 5	Thin film	57.3

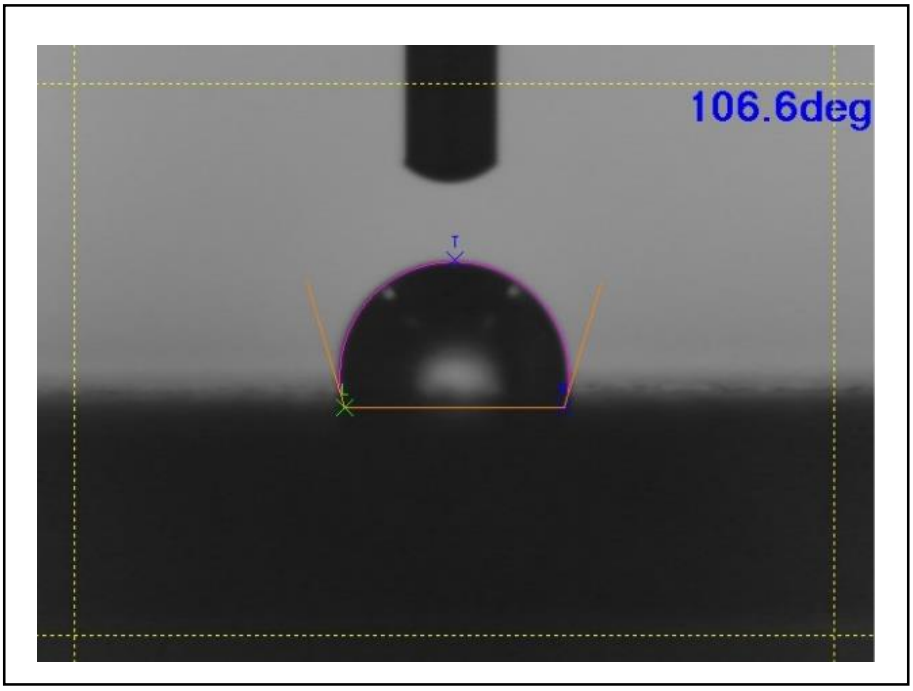


Figure 4.12 Foamy laminate contact angle measurement.

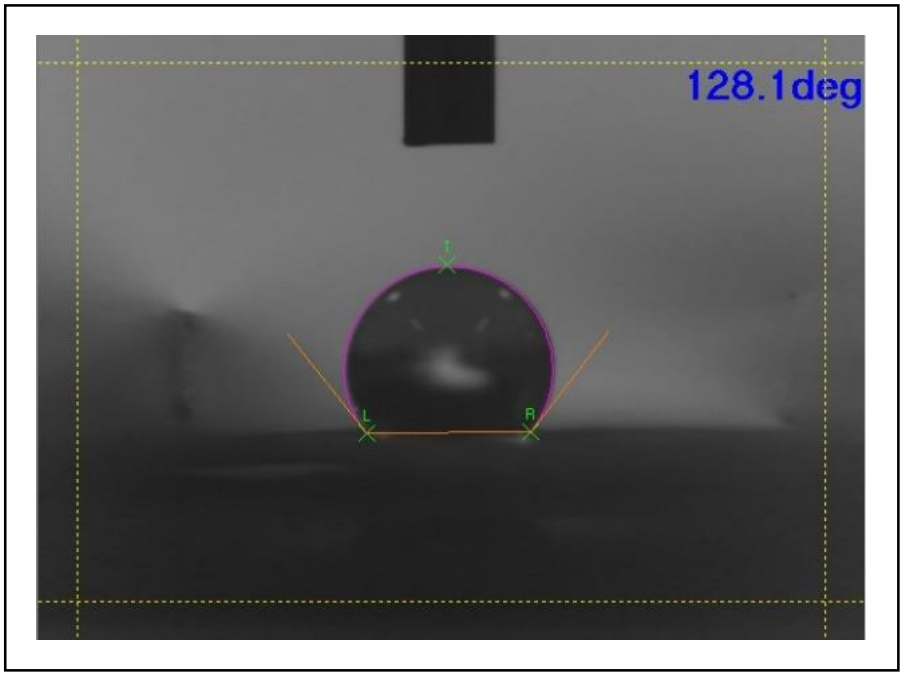


Figure 4.13 Electrospun nanofibers contact angle measurement.

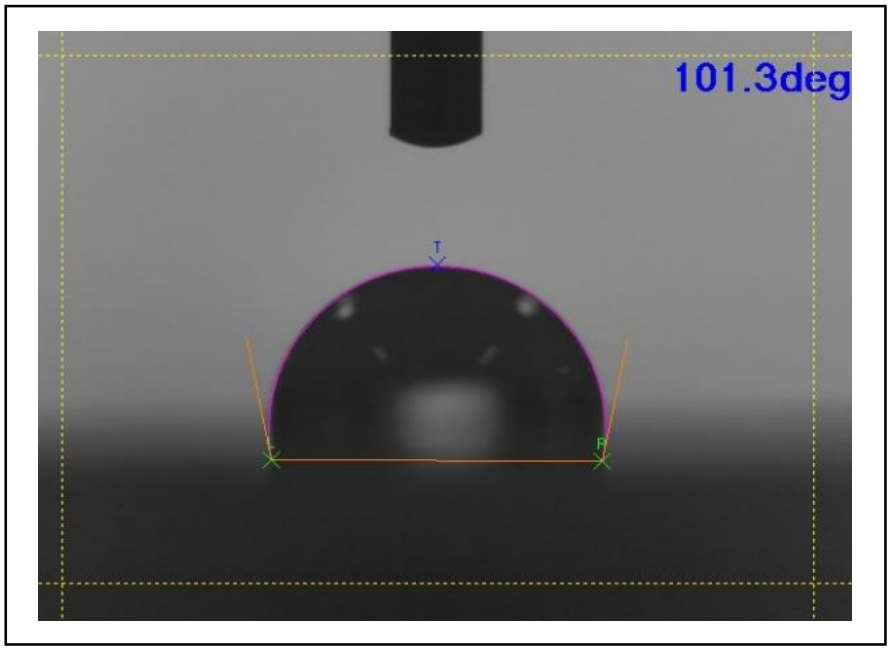


Figure 4.14 Multi-laminar composite with rubbery interface contact angle measurement.

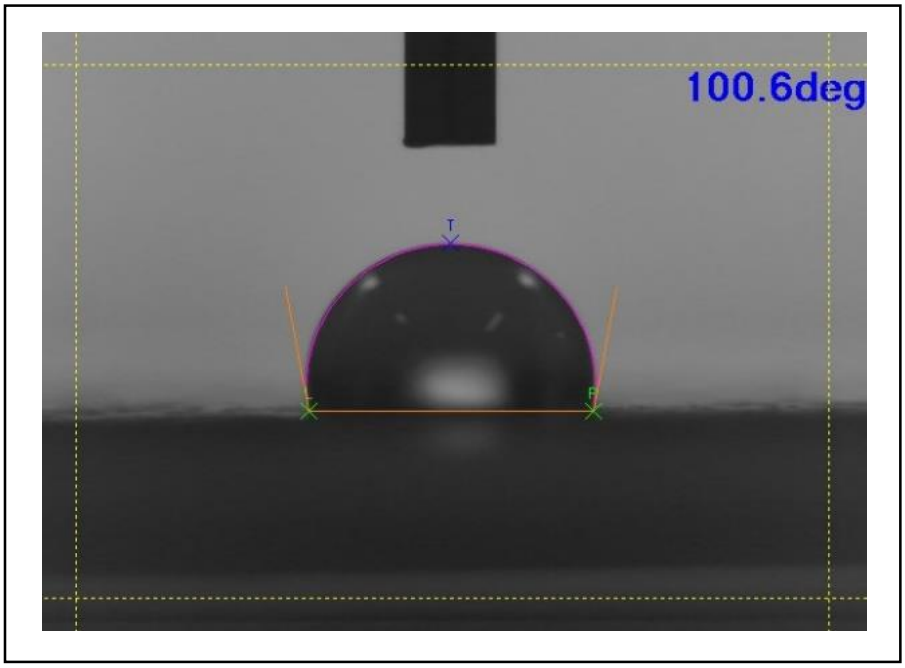


Figure 4.15 Deformable foamy laminate contact angle measurement.

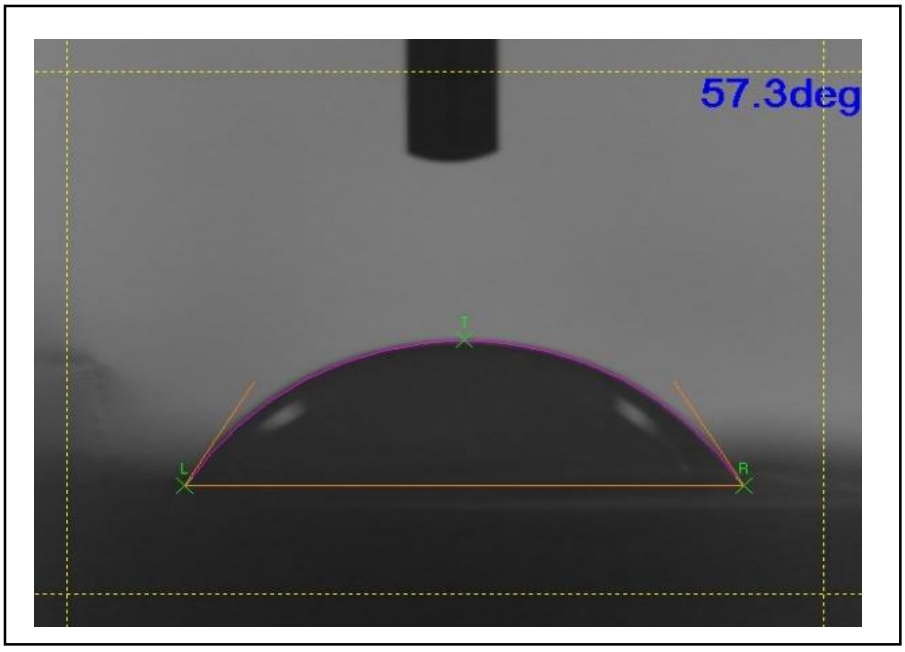


Figure 4.16 Thin film adhesive contact angle.

4.4 Samples Delamination

After evaluating all the previous parameters, the delamination of the samples was observed and analyzed under the optical microscope.

4.4.1 Foamy Laminate

The foamy laminate was delaminated from the substrate and the progressive delamination front is represented by the vertical blue line from left to right.

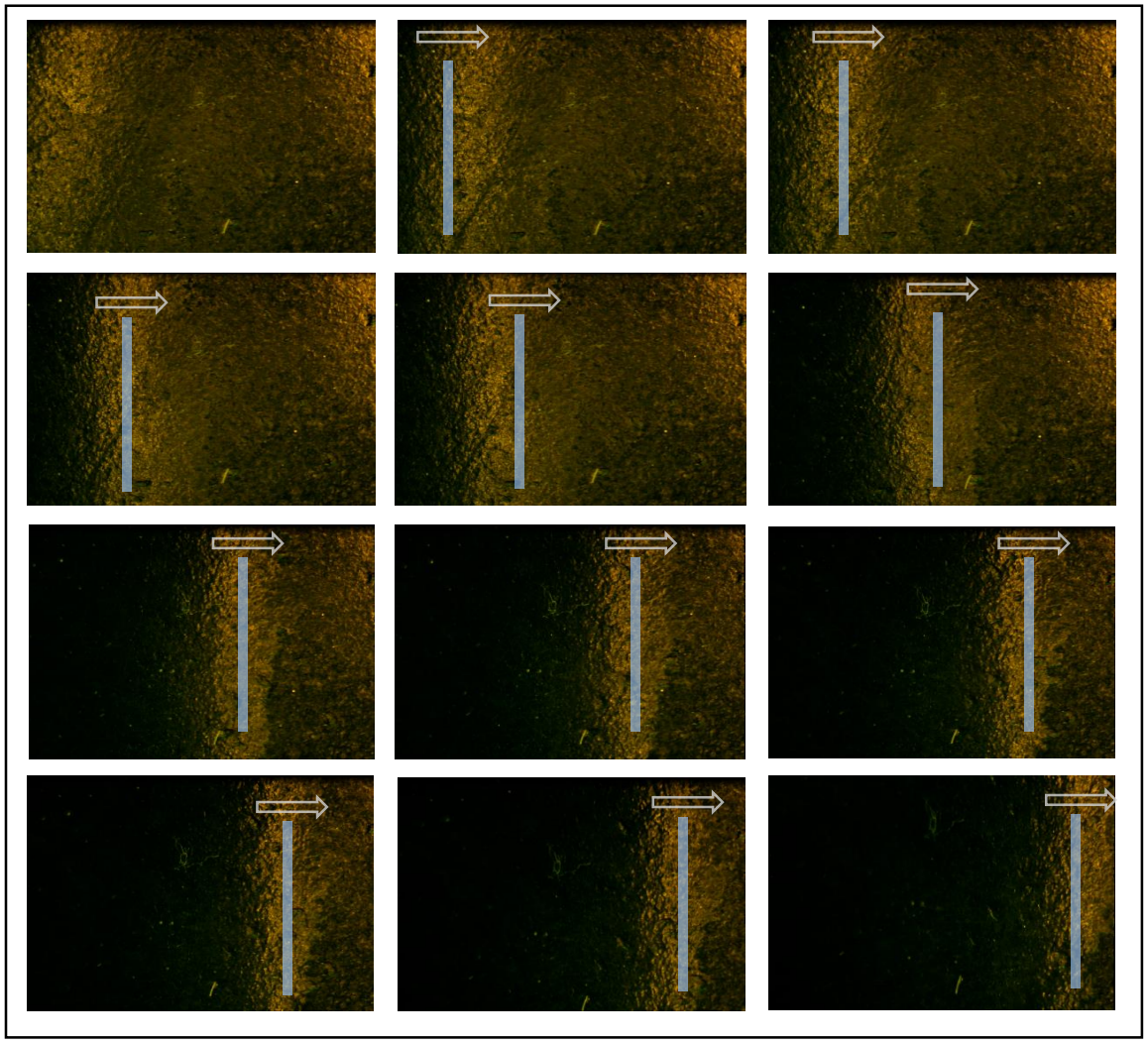


Figure 4.17 Delamination process of the foamy laminate adhesive.

Figure 4.17 shows how the foamy laminate adhesive is being delaminated, it is clear to see how the sample delaminates without stretching the adhesive material and the foamy laminate.

It can be seeing in the first frame of figure 4.17 that the sample is laminated and is in almost uniform interfacial contact with the substrate surface, from the following frames is seeing how the adhesive and the foamy layer behaves as a whole system.

The foamy layer is used not just as a reinforcement in this system, it is used also as a conforming interface for the adhesive layer to enhance interfacial contact between the sample and the substrate surface.

4.4.2 Multi-Laminar Composite with Rubbery Interface

Figure 4.18 shows the delamination process of the multi-laminar composite with a rubbery interface, this system after being conformed to a substrate with certain roughness or asperities starts to auto-delaminate. This is due the stiffness that the multi-laminar reinforcement brings to the system, and the high viscoelasticity of the adhesive layer.

This adhesive system presents a very poor performance when is laminated in irregular surfaces or when changes in the geometry of the adherend are present. The best performance can be obtained from flat uniform surfaces free of intrusions and extrusions.

The laminar reinforcement compromise the performance of the adhesive interface, hence from the whole adhesive system.

Figure 4.18 Delamination process of Multi-laminar composite with rubbery interface adhesive.

From the first frame of figure 4.18 sample is completed laminated, starting a simultaneous delamination from frame two, until completely delaminates in the last frame.

4.4.3 Deformable Foamy Laminate

Figure 4.19 shows the delamination process of deformable foamy laminate adhesive. Red discontinuous line represents the edge of the sample, black discontinuous line represents the reduction in width, and the purple arc represents the delamination progress.

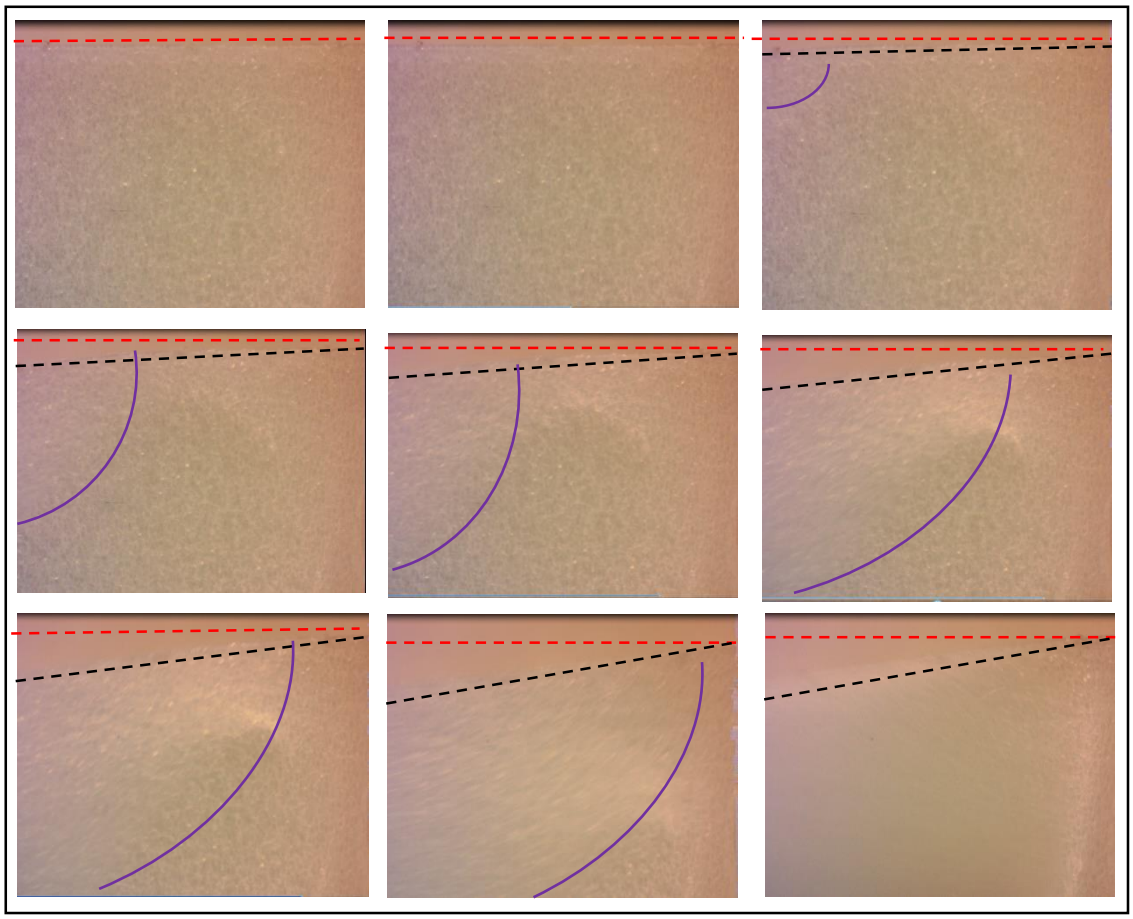


Figure 4.19 Delamination process of deformable foamy laminate adhesive.

It is possible to see how the facestock starts to reduce width, while being delaminating, this low loading plastic deformation is possible due the aligned micro voids presented in the structure of the facestock showed in figures 4.10 and 4.11.

4.4.4 Electrospun Fibers

Figure 4.20 shows the lamination and delamination process of the electrospun nanofibers, it was found that the electrospun nanofibers once laminated in the facestock, the fibers did not delaminate or auto-delaminate like the samples discussed in the previous section, it's also possible to see the surface of the adhesive system is not a flat smooth surface, instead presents a well-defined rough linear pattern.

Figure 4.20 Delamination process of electrospun nanofibers. (A) Lamination of the sample from right to left on the substrate, (B) Delamination of the sample from left to right.

During the lamination process is possible to see how the fibers conform to the surface of the adherend, modifying the surface from a rough interface to a considerable smooth surface, all the internal voids and air pockets are being reduced during lamination.

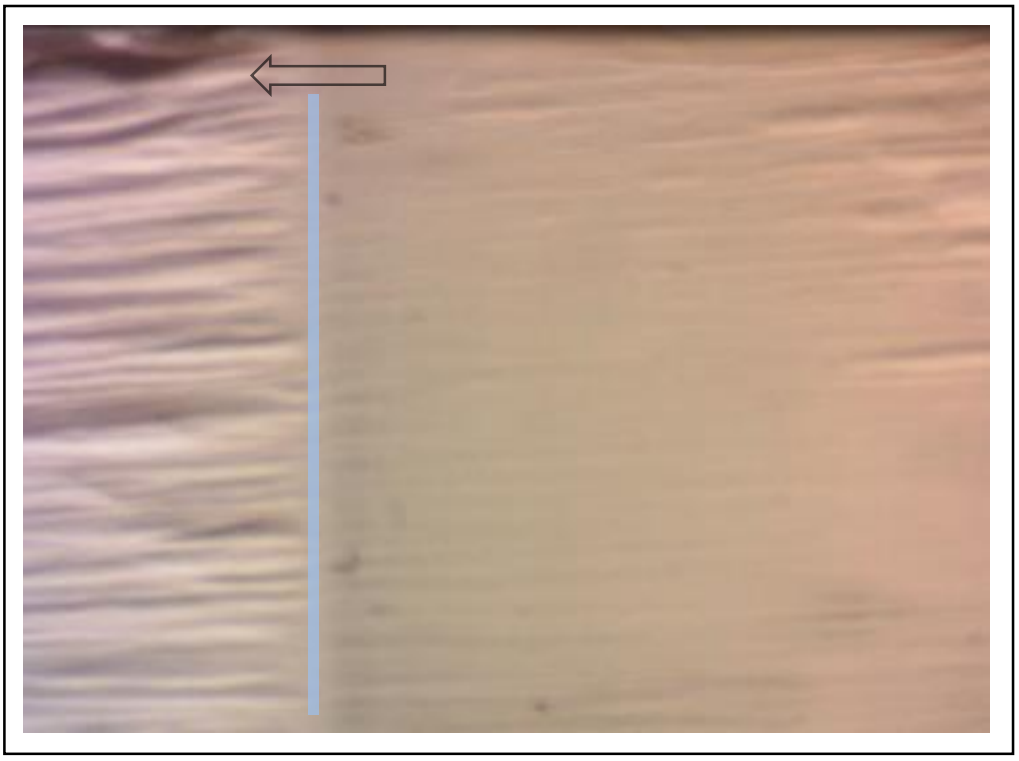


Figure 4.21 Surface roughness reduction during lamination.

It is possible to see in figure 4.21 a well-defined boundary between the the laminated and the not laminated part of the sample. In the samples discussed in the previous sections it is possible to see how the adhesive in a liquid state wets the surface, for this case the nanofibers conform to the substrate in a solid/dry state.

Figure 4.22 shows the delamination process of the nanofibers. It is possible to see that the sample doesn't delaminate as a whole system, in the lower half of the sample with discontinuous black lines are marked the fibers that are still laminated during the delamination process

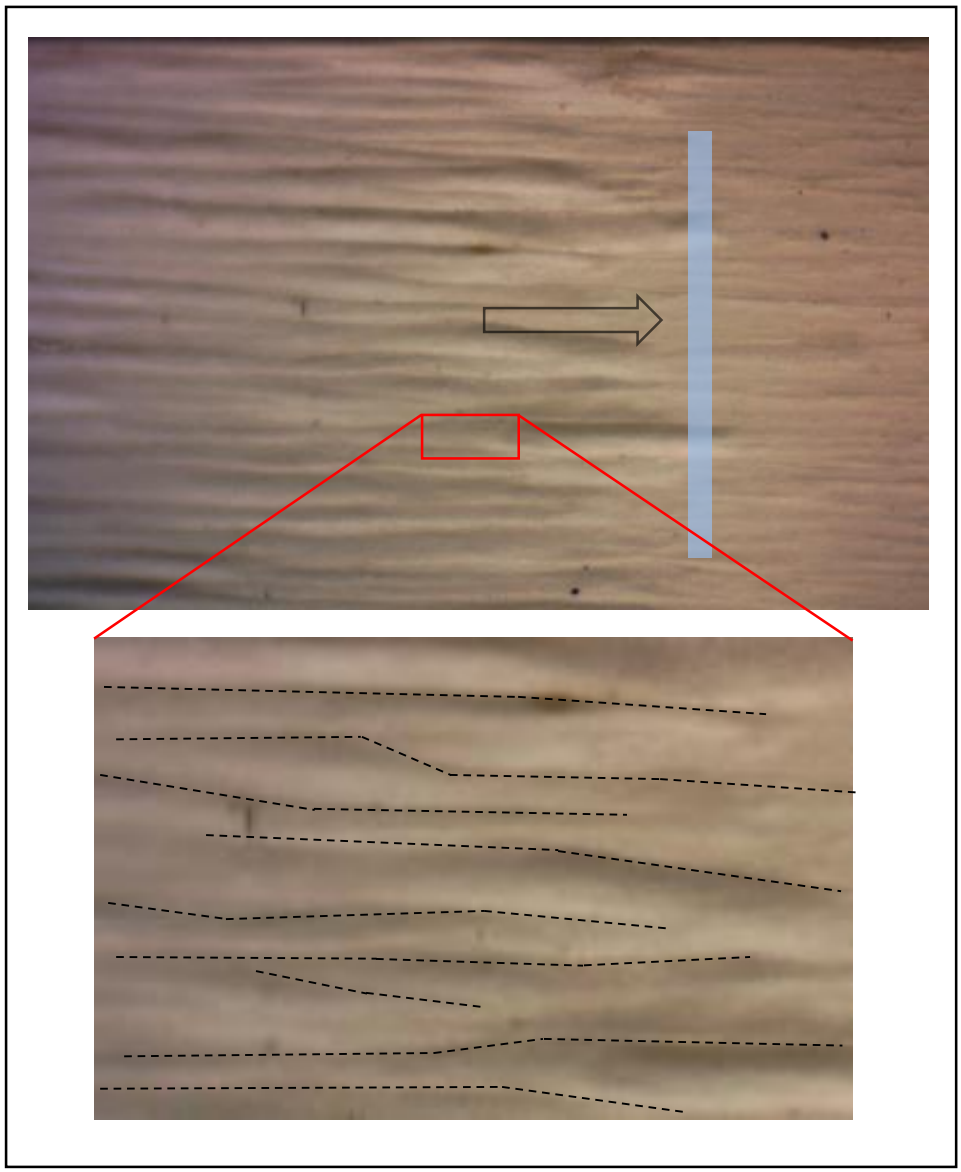


Figure 4.22 Independent fibers delamination.

CHAPTER V

CONCLUSIONS

5.1 Conclusions

After analyzing and comparing the delamination behavior of the electrospun nanofiber dry adhesives and the current generation of commercially available repositionable adhesives, it is possible to conclude the following:

- For the commercially available repositionable adhesives, delamination occurs as a system-wide process due to both the high coherence of the adhesive layer and the rigidity of the facestock used in the laminate construction.
- In contrast to the commercial repositionable adhesives, the electrospun nanofiber adhesives behave as a multi-fibrillar structure consisting of nanofibers that can individually deform, adhere, and peel off at the nano/micro-scale.
- The adhesion strength of the multi-fibrillar adhesive system is not determined by any specific chemical interaction or liquid wetting phenomena, such as in commercial adhesives, but rather from molecular interaction and attraction forces (van der Waals) between the surface of the substrate and the nanofibers.
- The adhesion strength of the electrospun nanofibers is strongly related to the interfacial contact points between the nanofibers and the substrate, as well as the porosity of the electrospun fiber mat. The porosity does introduce flaw and crack

initiation sites that may reduce the cohesive energy of the adhesive, but more importantly, it increases the compliance of the adhesive system, which facilitates conformation of the surface to the substrate and thereby increases the true contact area.

- The electrospun nanofibers show a unique combination of high shear strength and low peeling force that can be attributed to the length scale of the individual nanofibers and the specific adhesive mechanisms active in the system, in particular friction and mechanical interlocking with the substrate. Shear strength is dependent on the contact area between the adhesive objects and the substrates, which is considerable for each nanofiber because of their extreme length. Peel strength is dependent on only the contact width, which is extremely small for the individual nanofibers. As a result, the bulk adhesive is easily peeled from the surface, which provides both reusability and repositionability in applications.
- The conformation of the nanofibers to surface asperities along the substrate also generates a nano/micro mechanical interlocking mechanism that contributes to the adhesion strength. Mechanical interlocking will be most effective in shear and will not contribute to an increase in peel strength, which further increases the anisotropy in adhesive strength for this new class of adhesives.

REFERENCES

[1] Täljsten. (2006). The importance of bonding–a historic overview and future possibilities. Advances in Structural Engineering, 9(6), 721-736.

[2] Mazza, P; Martini, F; Sala, B; Magi, M; Colombini, M; Giachi, G; Landucci, F; Lemorini, C; Modugno, F; Ribechini, E (January 2006). "A new Palaeolithic discovery: tar-hafted stone tools in a European Mid-Pleistocene bone-bearing bed". *Journal of Archaeological Science* **33** (9): 1310.

[3] Wu, S. (1982). Polymer interface and adhesion. M. Dekker.

[4] Graham, L. D. (2008). Biological adhesives from nature. Encyclopedia of biomaterials and biomedical engineering, 1, 236-253.

[5] Kinloch, A. (2012). Adhesion and adhesives: science and technology. Springer Science & Business Media.

[6] Varenberg, M., Pugno, N. M., & Gorb, S. N. (2010). Spatulate structures in biological fibrillar adhesion. Soft Matter, 6(14), 3269-3272.

[7] Lee, H., Lee, B. P., & Messersmith, P. B. (2007). A reversible wet/dry adhesive inspired by mussels and geckos. Nature, 448(7151), 338-341.

[8] Shi, Q., Wan, K. T., Wong, S. C., Chen, P., & Blackledge, T. A. (2010). Do electrospun polymer fibers stick?. *Langmuir*, *26*(17), 14188-14193.

[9] Shi, Q., Wong, S. C., Ye, W., Hou, J., Zhao, J., & Yin, J. (2012). Mechanism of adhesion between polymer fibers at nanoscale contacts. *Langmuir*, *28*(10), 4663-4671.

[10] Wang, X., Najem, J. F., Wong, S. C., & Wan, K. T. (2012). A nano-cheese-cutter to directly measure interfacial adhesion of freestanding nano-fibers. *Journal of Applied Physics*, *111*(2), 024315.

[11] Na, H., Chen, P., Wan, K. T., Wong, S. C., Li, Q., & Ma, Z. (2012). Measurement of adhesion work of electrospun polymer membrane by shaft-loaded blister test. *Langmuir*, *28*(16), 6677-6683.

[12] Najem, J. F., Wong, S. C., & Ji, G. (2014). Shear Adhesion Strength of Aligned Electrospun Nanofibers. *Langmuir*, *30*(34), 10410-10418.

[13] Ji, G., Wong, S. C., Ma, X., & Blackledge, T. A. (2014, February). Adhesion of Electrospun Polymer Blends. In *Proceedings of the 37th Annual Meeting of the Adhesion Society* (pp. 23-26).

[14] Wong, S. C., & Najem, J. F. (2013, October). Polymeric fiber arrays for adhesion. In *ICF13*.

[15] Wong, Shing Chung Josh; Najem, Johnny F.; and Chen, Pei, "Fabrication of Nanofibers as Dry Adhesives and Applications of the Same" (2014). *Department of Mechanical Engineering.* Paper 582.

[16] Davis, J. R. (Ed.). (1992). *ASM materials engineering dictionary*. ASM international.

[17] Landrock, A. H., & Ebnesajjad, S. (2008). *Adhesives technology handbook*. William Andrew.

[18] Troughton, M. J. (2008). *Handbook of plastics joining: a practical guide*. William Andrew.

[19] Johnston, J. (2000). Pressure sensitive adhesive tapes: A guide to their function, design, manufacture, and use.

[20] ASTM D 1878-61 T, ASTM Bull. No. 221,64 (1957).

[21] Benedek, I. (2004). *Pressure-sensitive adhesives and applications*. CRC Press.

[22] da Silva, L. F. M. (Ed.). (2011). *Handbook of adhesion technology: with 97 tables*. Springer Science & Business Media.

[23] Favi, P. M., Yi, S., Lenaghan, S. C., Xia, L., & Zhang, M. (2014). Inspiration from the natural world: from bio-adhesives to bio-inspired adhesives. *Journal of Adhesion Science and Technology*, *28*(3-4), 290-319.

[24] Tschegg, S. E., & Seidel, R. (Eds.). (2010). *Proceedings of the COST Strategic Workshop Principles and Development of Bio-Inspired Materials, Vienna, 13-15 April 2010*. BOKU-University of natural resources and applied life sciences.

[25] L. F. Boesel, C. Greiner, E. Arzt, A. del Campo, *Gecko-inspired surfaces: a path to strong and reversible dry adhesives*, Adv. Mater., (2009).

[26] Favi, P. M., Yi, S., Lenaghan, S. C., Xia, L., & Zhang, M. (2014). Inspiration from the natural world: from bio-adhesives to bio-inspired adhesives. *Journal of Adhesion Science and Technology*, *28*(3-4), 290-319.
[27] Autumn, K., Sitti, M., Liang, Y. A., Peattie, A. M., Hansen, W. R., Sponberg, S., ... & Full, R. J. (2002). Evidence for van der Waals adhesion in gecko setae. *Proceedings of the National Academy of Sciences*, *99*(19), 12252-12256.

[28] Zhang, X., Liu, Y., Liu, Y., & Ahmed, S. U. (2009). Controllable and switchable capillary adhesion mechanism for bio-adhesive pads: Effect of micro patterns. *Chinese Science Bulletin*, *54*(10), 1648-1654.

[29] Monahan, J., & Wilker, J. J. (2004). Cross-linking the protein precursor of marine mussel adhesives: bulk measurements and reagents for curing. *Langmuir*, *20*(9), 3724-3729.

[30] Cha, H. J., Hwang, D. S., & Lim, S. (2008). Development of bioadhesives from marine mussels. *Biotechnology journal*, *3*(5), 631.

[31] Hansen, W. R., & Autumn, K. (2005). Evidence for self-cleaning in gecko setae. *Proceedings of the National Academy of Sciences of the United States of America*, *102*(2), 385-389.

[32] Gorb, S. N., Sinha, M., Peressadko, A., Daltorio, K. A., & Quinn, R. D. (2007). Insects did it first: a micropatterned adhesive tape for robotic applications. *Bioinspiration & biomimetics*, *2*(4), S117.

[33] Gorb, S. N. (2008). Biological attachment devices: exploring nature's diversity for biomimetics. *Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*, *366*(1870), 1557-1574.

[34] Cognard, P. (2006). Adhesives and Sealants: General Knowledge, Application Techniques, New Curing Techniques: General Knowledge, Application of Adhesives, New Curing Techniques In: Handbook of adhesives and sealants. *Gebundene Ausgabe von Philippe Cognard von Elsevier Science & Technology*.

[35] Jewett, J. W., Serway, R. A., & Peroomian, V. (2010). *Physics for scientists and engineers*. Brooks/Cole.

[36] Cognard, P. (2006). *Handbook of Adhesives and Sealants: General Knowledge, Application of Adhesives, New Curing Techniques* (Vol. 2). Elsevier.

[37] Mittal, K. L., & Pizzi, A. (Eds.). (1999). *Adhesion promotion techniques: technological applications*. CRC Press.

[38] Kang, E. T., Neoh, K. G., Tan, K. L., & Liaw, D. J. (1999). Adhesion Promotion Techniques: Technological Applications.

[39] Vasenin, R. M. (1969). Adhesion, Fundamentals and Practice. *Ministry of Technology, MacLaren, London*.

[40] Hildebrand, J., Scott, R., *The Solubility of Non-Electrolytes*, 3rd. Ed. (1950). Reinhold, New York.

[41] Gierenz, G., & Karmann, W. (Eds.). (2008). *Adhesives and adhesive tapes*. John Wiley & Sons.

[42] Derjaguin, B. V., & Smilga, V. P. (1967). Electronic theory of adhesion. *Journal of Applied Physics*, *38*(12), 4609-4616.

[43] McBain, J. W.; Hopkins, D. G. J. Phys. Chem. 1925, 29, 188.

[44] Bikerman, J. J. (2013). *The science of adhesive joints*. Elsevier.

[45] Arzt, E., Gorb, S., & Spolenak, R. (2003). From micro to nano contacts in biological attachment devices. Proceedings of the National Academy of Sciences, 100(19), 10603-10606.

[46] Del Campo, A., Greiner, C., & Arzt, E. (2007). Contact shape controls adhesion of bioinspired fibrillar surfaces. Langmuir, 23(20), 10235-10243.

[47] Sitti, M., & Fearing, R. S. (2003). Synthetic gecko foot-hair micro/nano-structures as dry adhesives. *Journal of Adhesion Science and Technology*, *17*(8), 1055-1073.

[48] Kim, D. S., Lee, H. S., Lee, J., Kim, S., Lee, K. H., Moon, W., & Kwon, T. H. (2007). Replication of high-aspect-ratio nanopillar array for biomimetic gecko foot-hair prototype by UV nano embossing with anodic aluminum oxide mold. *Microsystem Technologies*, *13*(5-6), 601-606.

[49] Zhao, Y., Tong, T., Delzeit, L., Kashani, A., Meyyappan, M., & Majumdar, A. (2006). Interfacial energy and strength of multiwalled-carbon-nanotube-based dry adhesive. Journal of Vacuum Science & Technology B, 24(1), 331-335.

[50] Ge, L., Sethi, S., Ci, L., Ajayan, P. M., & Dhinojwala, A. (2007). Carbon nanotube-based synthetic gecko tapes. Proceedings of the National Academy of Sciences, 104(26), 10792-10795.

[51] Qu, L., Dai, L., Stone, M., Xia, Z., & Wang, Z. L. (2008). Carbon nanotube arrays with strong shear binding-on and easy normal lifting-off. Science,322(5899), 238-242.

[52] Notargiacomo, A., Foglietti, V., Cianci, E., Capellini, G., Adami, M., Faraci, P., ... & Nicolini, C. (1999). Atomic force microscopy lithography as a nanodevice development technique*. Nanotechnology, 10(4), 458.
[53] Liu, S., Zhang, P., Lü, H., Zhang, C., & Xia, Q. (2012). Fabrication of high aspect ratio microfiber arrays that mimic gecko foot hairs. Chinese Science Bulletin, 57(4), 404-408.

[54] Geim, A. K., Dubonos, S. V., Grigorieva, I. V., Novoselov, K. S., Zhukov, A. A., & Shapoval, S. Y. (2003). Microfabricated adhesive mimicking gecko foot-hair. Nature materials, 2(7), 461-463.

[55] Lee, H., Lee, B. P., & Messersmith, P. B. (2007). A reversible wet/dry adhesive inspired by mussels and geckos. Nature, 448(7151), 338-341.

[56] Parness, A., Soto, D., Esparza, N., Gravish, N., Wilkinson, M., Autumn, K., & Cutkosky, M. (2009). A microfabricated wedge-shaped adhesive array displaying gecko-like dynamic adhesion, directionality and long lifetime. Journal of the Royal Society Interface, rsif-2009.

[57] Anton, F. (1934). U.S. Patent No. 1,975,504. Washington, DC: U.S. Patent and Trademark Office.

[58] Liu, Y., Mo, L. F., Wan, Y. Q., & Xu, L. (2008). Electrospun nanofibres and their applications. Shawbury, UK: ISmithers.

[59] Wang, Z. L. (2000). Characterizing the structure and properties of individual wire-like nanoentities. Advanced Materials, 12(17), 1295-1298.

[60] Doshi J, Reneker DH (1995) Electrospinning process and applications of electrospun fibers. J Electrostat 35(2–3):151–160.

[61] Reneker DH, Chun I (1996) Nanometre diameter fibres of polymer, produced by electrospinning. Nanotechnology 7(3):216–223.

[62] Deitzel, J. M., Kleinmeyer, J., Harris, D. E. A., & Tan, N. B. (2001). The effect of processing variables on the morphology of electrospun nanofibers and textiles. Polymer, 42(1), 261-272.

[63] Fong, H., Chun, I., & Reneker, D. H. (1999). Beaded nanofibers formed during electrospinning. Polymer, 40(16), 4585-4592.

[64] Yang, Q., Li, Z., Hong, Y., Zhao, Y., Qiu, S., Wang, C. E., & Wei, Y. (2004). Influence of solvents on the formation of ultrathin uniform poly (vinyl pyrrolidone)

nanofibers with electrospinning. Journal of Polymer Science Part B: Polymer Physics, 42(20), 3721-3726.

[65] Demir, M. M., Yilgor, I., Yilgor, E. E. A., & Erman, B. (2002). Electrospinning of polyurethane fibers. *Polymer*, *43*(11), 3303-3309.
[66] Deitzel, J. M., Kleinmeyer, J., Harris, D. E. A., & Tan, N. B. (2001). The effect of processing variables on the morphology of electrospun nanofibers and textiles. *Polymer*, *42*(1), 261-272.

[67] Koski A, Yim K, Shivkumar S (2004) Effect of molecular weight on fibrous PVA produced by electrospinning. Mater Lett 58 (3–4):493–497.

[68] Ko, F. K. (2006). Q Nanofiber Technology. *Nanotubes and Nanofibers*, 233.

[69] Lin, Z. et al. (2010). J. Appl. Polym. Sci., 116, p.895.

[70] Terada, D., Kobayashi, H., Zhang, K., Tiwari, A., Yoshikawa, C., & Hanagata, N. (2012). Transient charge-masking effect of applied voltage on electrospinning of pure chitosan nanofibers from aqueous solutions. *Science and Technology of Advanced Materials*, *13*(1), 015003.

[71] Koombhongse, P. (2006). Effect of Solvent on Morphology of Electrospun Polystyrene Nanofiber.

[72] Angammana, C. J., & Jayaram, S. H. (2011). Analysis of the effects of solution conductivity on electrospinning process and fiber morphology. *Industry Applications, IEEE Transactions on*, *47*(3), 1109-1117.

[73] Huang, C., Chen, S., Lai, C., Reneker, D. H., Qiu, H., Ye, Y., & Hou, H. (2006).

[74] Lin, T. (2011). Nanofibers-production, properties and functional applications.

[75] Taylor, G. (1969, December). Electrically driven jets. In *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences* (Vol. 313, No. 1515, pp. 453-475). The Royal Society.

[76] Taylor, G. (1964, July). Disintegration of water drops in an electric field. In *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences* (Vol. 280, No. 1382, pp. 383-397). The Royal Society.

[77] Rangkupan, R., & Reneker, D. H. (2003). Electrospinning Process of Molten Polypropylene in Vacuum. *Journal of Metals, Materials and Minerals*, *12*(2), 81-87.

[78] Yuan, X., Zhang, Y., Dong, C., & Sheng, J. (2004). Morphology of ultrafine polysulfone fibers prepared by electrospinning. *Polymer International*, *53*(11), 1704-1710.

[79] Katta, P., Alessandro, M., Ramsier, R. D., & Chase, G. G. (2004). Continuous electrospinning of aligned polymer nanofibers onto a wire drum collector. Nano letters, 4(11), 2215-2218.

[80] Sundaray B, Subramanian V, Natarajan TS, Xiang R-Z, Chang C–C, Fann W-S (2004) Electrospinning of continuous aligned polymer fibers. Appl Phys Lett 84(7):1222–1224.

[81] Mit-uppatham, C., Nithitanakul, M., & Supaphol, P. (2004). Ultrafine electrospun polyamide-6 fibers: effect of solution conditions on morphology and average fiber diameter. Macromolecular Chemistry and Physics, 205(17), 2327-2338.

[82] Casper, C. L., Stephens, J. S., Tassi, N. G., Chase, D. B., & Rabolt, J. F. (2004). Controlling surface morphology of electrospun polystyrene fibers: effect of humidity and molecular weight in the electrospinning process. Macromolecules, 37(2), 573-578.

[83] Mittal, K. L. (Ed.). (2006). Contact angle, wettability and adhesion (Vol. 4). CRC Press.

[84] Young, T. (1805). Phil. Trans Roy. Soc, 95, 65-75.

[85] Nuraje, N., Khan, W. S., Lei, Y., Ceylan, M., & Asmatulu, R. (2013). Superhydrophobic electrospun nanofibers. Journal of Materials Chemistry A, 1(6), 1929-1946.

[86] Burchardt, B. (2011). Automotive Industry. In *Handbook of Adhesion Technology* (pp. 1185-1212). Springer Berlin Heidelberg.

[87] Cognard, P. (2006). *Handbook of Adhesives and Sealants: General Knowledge, Application of Adhesives, New Curing Techniques* (Vol. 2). Elsevier.

[88] Krieger Jr, R. B. (1979). Fatigue testing of structural adhesives. *Structural Adhesives and Bonding*, 48-71.

[89] Custódio, J., Broughton, J., Cruz, H., & Winfield, P. (2009). Activation of timber surfaces by flame and corona treatments to improve adhesion. *International Journal of Adhesion and Adhesives*, *29*(2), 167-172.

[90] Albrecht, P., Sahli, A., Crute, D., Albrecht, P., & Evans, B. (1984). *Application of adhesives to steel bridges* (No. FHWA-RD-84-037 Final Rpt.).

[91] Ferrier, E., Lagarde, G., & Hamelin, P. (2001). Concrete beams reinforced by fibre-reinforced plastics: the effect of temperature on the adhesive layer.*Composites science and technology*, *61*(3), 425-431.

[92] Meier, U. (1994). Rehabilitation of structures with the CFRP sheet bonding technique. *Advancing with composites*, *94*, 169-181.
[93] Tavakoli, S. M. (2002). Adhesive bonding of medical and implantable devices.*Medical device technology*, *13*(7), 32-36.

[94] Manfroy, P. P., Ashton-Miller, J. A., & Wojtys, E. M. (1997). The effect of exercise, prewrap, and athletic tape on the maximal active and passive ankle resistance to ankle inversion. *The American journal of sports medicine*, *25*(2), 156-163.

[95] Ewoldsen, N., & Demke, R. S. (2001). A review of orthodontic cements and adhesives. *American Journal of Orthodontics and Dentofacial Orthopedics*,*120*(1), 45-48.

[96] Gierenz, G., & Karmann, W. (Eds.). (2008). *Adhesives and adhesive tapes*. John Wiley & Sons.

[97] Johnston, J. (2000). Pressure sensitive adhesive tapes: A guide to their function, design, manufacture, and use.

[98] Walker, J. M. (Ed.). (1996). *Handbook of manufacturing engineering*. Marcel Dekker.

[99] Lu, D., Wong, C. P., & Tong, Q. K. (1998, March). A fundamental study on silver flakes for conductive adhesives. In *Advanced Packaging Materials, 1998. Proceedings. 1998 4th International Symposium on* (pp. 256-260). IEEE.

[100] Kristiansen, H., & Liu, J. (1998). Overview of conductive adhesive interconnection technologies for LCDs. *Components, Packaging, and Manufacturing Technology, Part A, IEEE Transactions on*, *21*(2), 208-214.

[101] Xu, S., Dillard, D. A., & Dillard, J. G. (2003). Environmental aging effects on the durability of electrically conductive adhesive joints. *International Journal of Adhesion and Adhesives*, *23*(3), 235-250.

[102] Singh, P., & Viswanadham, P. (2012). *Failure modes and mechanisms in electronic packages*. Springer Science & Business Media.

[103] Benedek, I. (2004). *Pressure-sensitive adhesives and applications*. CRC Press.

[104] Satas, D. (1989). *Handbook of pressure sensitive adhesive technology*. Van Nostrand Reinhold.